1977

Specific Determination of Airborne Sulfates and Sulfuric Acid.

Purnendu Kumar Dasgupta
Louisiana State University and Agricultural & Mechanical College

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SPECIFIC DETERMINATION OF AIRBORNE SULFATES AND SULFURIC ACID

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Purnendu Kumar Dasgupta
M.Sc. University of Burdwan, 1970
December, 1977

TO MY MOTHER

"...Every breeze that blows kindly is one crystal breath

We exhale on the blue diamond heaven

As gentle to touch as the hands of the healer

As soft as the farewells whispered over the coffin

We're poisoned with venom with each breath we take

From the brown sulphur chimney

And the black highway snake

...Every fish that swims silent, every bird that flies freely

Every doe that steps softly, every crisp leaf that falls

All the flowers that grow on this colorful tapestry

Somehow they know that if man is allowed to destroy all we need

He will soon have to pay with his life for his greed."

- Don McLean, Tapestry.

FOREWORD

The work described in this dissertation is neither ground breaking nor earth shaking, it merely represents the efforts of a man with limited intellect and ability to solve a problem which sorely needs a solution. There are no pretensions towards disseminating some fundamental scientific truth. Based on a new reaction, a new analytical method has been developed to determine aqueous and airborne sulfate at levels not conveniently determinable previously and a few new compounds have been synthesized and characterized. As the computer scientist would say, the program is different and better, but neither the hardware nor the language is new.

The scope of this work is almost entirely environmental. Environmental chemistry is a relatively new subject, at least as far as most chemists are concerned, and this author has had to educate himself on this subject largely on his own. The study of the environment is multi-faceted; physics of the atmosphere, chemistry of trace substances in our air and water, toxicology at trace levels, health related epidemiological studies - these subjects are all intimately related. In the concerted effort the chemist's role is not any less important than that of anyone else.

After all the supreme harmony is in complete interdependence. A great amount of time and effort has been spent to prepare the first part of the dissertation in which the nature of the problem is described. Extensive references that cover all the salient points have been given; some historical references have been given

along with the scientific ones but the list of references is not an exhaustive one except in Chapter V, where every effort has been made to cover in understandable detail, all the methods that are currently used to determine airborne sulfuric acid and sulfates. At the end of the reference section a bar graph depicts the frequency of the literature cited in this dissertation vs. the year of publication; if it does nothing else, this would serve to indicate mankind's increasing interest in the science of the environment.

The effort to write such a detailed introductory part stems simply from the feeling that at the present time if there is any purpose in writing dissertations beyond binding an identical copy of the manuscript/s sent to journals between some other typed sheets, it must justify itself. This feeling does not imply that the experimental section does not take precedence. This is a dissertation in analytical chemistry. And chemistry is an experimental science.

The author wishes to acknowledge the man who made him truly understand that chemistry is still an experimental science. To paraphrase Dylan, the author gratefully acknowledges the very humane scientist Philip W. West because --- "He said, I'll give you a shelter from the storm." He gave the author a chance to work independently on a challenging problem and offered help and suggestions whenever it was needed. And above all, he irrevocably and undefinably touched the molding of the author's thought process.

It is true that we pay a price for everything we do. The

impact of industrialization on the environment would never be a rectified positive wave. We should be ready to pay the price for necessary progress but the word progress sometimes is difficult to define.

A latest best-selling self-heating shave cream bears the following list of ingredients: water, stearic acid, triethanolamine, 1,5-diethyl-4-hydroxy-2-mercapto-6-oxopyrimidine, isobutane, Laureth-23, potassium hydroxide, sorbitol, hydrogen peroxide, sodium lauryl sarcosinate, propane, fragrance, lauramine oxide, potassium silicate, butane, ammonium molybdate, phenacetin, and sodium stannate. Even if a shaving cream that heats itself can be considered necessary progress, does anyone know what price he is really paying?

The help, advice and the suggestions of many people made this work possible. Drs. K. D. Reiszner and G. L. Lundquist were invaluable. The comradeship of D. L. McDermott and earlier, H. F. Merrick in the laboratory has been a great experience. Dr. W. D. Pitts took the enormous trouble of reading and correcting the entire dissertation in its handwritten (hieroglyphic) form. The same magical reading ability was displayed by Betty Stubbs who managed to type it.

There are few people in the Chemistry Department whom this author did not bother with his problems during one or another facet of this work. First, the help of Drs. G. R. Newkome and A. Nayak in structural studies must be cited. Our resident electronic experts G. H. Sexton and especially L. S. Edelen willingly provided their

expertise whenever asked. Our talented computer programmer Alex Nicolson bore the main burden of formulation and execution of the computer programs used in this study. L. G. P. Hanley Jr. was of inestimable help in rechecking and gathering substantial amounts of reported data. S. Bhattacharya and G. Gor made possible the digitization of the data necessary for the first 3-D plot that involved some 2600 points. The author would also like to thank the Library personnel, especially Mrs. B. Brown, who went to a great amount of trouble to hunt obscure material. Further acknowledgements for specific experimental help have been mentioned in the opening chapter of the experimental section.

The author wishes to acknowledge his debt to the Department of Chemistry for granting a teaching assistantship which made his pursuit of a doctoral degree possible in the first place and also to the Coates Memorial Fund which bore a part of the cost of preparation of this dissertation.

Lastly and very importantly, the author wants to say that he sincerely wishes he could alleviate the patient pain his family bore during these years and he has no words to express his feelings for his best friends, Wilson Gautreaux, Dr. Gail Smith, and Hunter Moles, who made his sane survival possible in this period.

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ABSTRACT

A method to determine trace levels or airborne sulfuric acid in the ambient atmosphere has been developed. It is possible to differentiate sulfuric acid from concommitantly present ammonium sulfate by means of this procedure. The procedure is spectrophotometric and a detection limit of 100 ng sulfate has been achieved. The method has also been applied to aqueous samples and a limit of detection of 5 ng sulfate has been achieved by ring oven techniques.

Glassfiber filters impregnated with 2-perimidinyl ammonium bromide are utilized in this method. Prior to filtration, the air stream is subjected to controlled heating to maintain a 40% relative humidity. At this humidity level sulfuric acid (and ammonium bisulfate) are collected as liquid aerosols and all other atmospherically important sulfate and bisulfate salts are collected as solid particulates. The liquid droplets of sulfuric acid react topochemically with the impregnating reagent to form the corresponding sulfate. The filter is then treated with a saturated solution of barium acetate in 75% acetone-25% methanol (v/v) which converts the particulate sulfates (notably ammonium sulfate) to barium sulfate. Subsequently the material on the filter is chromatographed and methanol is used as the eluting solvent. The filter is then treated with concentrated nitric acid upon which the organic amine, bound as sulfate, reacts to form 2-amino, 4,6,9-trinitroperimidine. This compound is intensely colored and

behaves as an acid-base indicator. After adding excess base the absorbance of the resulting solution is measured at 550 nm.

This dissertation also includes a detailed introduction to the general problem of airborne sulfate and sulfuric acid pollution. Pathways for the formation of atmospheric sulfates, toxicological evaluation of sulfuric acid and its salts, and the need for an ambient air quality standard for these species are discussed. In depth reviews of available methods for the determination of sulfuric acid and sulfates in air and water are included.

The chemistry of a class of new compounds, nitro substituted 2-aminoperimidines, which form the basis of the measurement method have also been described in this work. Thermal, spectral and polarographic data for five new compounds belonging to this family are given.

CHAPTER I

THE ATMOSPHERE, AIR POLLUTION AND AEROSOLS

"The most excellent canopy, the air - why it appears no other thing to me than a foul and pestilent congregation of vapours!"

- Shakespeare, Hamlet

The Atmosphere

The planet earth is enveloped by gases extending to a height of approximately 2000 km. The density decreases rapidly with increasing altitude; half the total mass of the atmosphere (estimated to be a total of 5.2×10^{15} Mtons) is contained within the lower 5 km. The variation of temperature gradient with altitude is used to subdivide the atmosphere into layers. The lowest part of the atmosphere, called the troposphere, is characterized by a negative temperature gradient of about 6°C/km. Next there is a zero gradient layer called the tropopause. The stratosphere comes next and has a positive temperature gradient. There follows rather abruptly an inversion layer (stratopause) which provides a transition to the mesophere where the temperature gradient is negative. The mesophere in turn is followed by the mesopause and then finally the thermosphere that extends upwards from about 90 km and has a steady and relatively high positive temperature gradient.

The troposphere interests us most because it contains all the air we breathe, use, abuse, and is the region in which all the weather processes occur. Mixing of the air mass within the troposphere in either the northern or southern hemisphere requires weeks whereas intermixing between the hemispheres requires years. The mixing time is significant since the quantity of man made material put into the air of the northern hemisphere is vastly different from that put into the air of the southern hemisphere. The exchange between the troposphere and the stratosphere is also

relatively slow and it is estimated that months are required to complete the exchange. Transfer into the stratosphere occurs mostly at the tropical tropopause while transfer into the troposphere takes place primarily at the mid-latitude tropopause.

Compared to the troposphere, mixing within the stratosphere is much more rapid, both in vertical and horizontal directions.

Air Pollutants

It obviously becomes necessary to define unpolluted air before one can define air pollutants. "Clean Air" compositions, based on measurements at sites distant from places of human activity or other 'abnormal' influences have been given by several authorities.[278,466] The purist's definition of an air pollutant is now obvious, an attitude characterized by the definition given by West German technical directives (TAL): "Solid, liquid or gaseous substances changing the natural composition of the atmosphere." Such a definition is so all inclusive that it is difficult to use rationally. Furthermore, there are no limits to which the purist may strive to achieve "purity", in spite of the fact that the composition of "Clean Air" may have changed during such an attempt. Almost all compositions of 'clean air' given by authorities do not include water vapor. It is an established fact that completely dry air, irrespective of its purity, is far more damaging to the human respiratory system than substantially polluted urban air. The goal of an environmentalist therefore should not necessarily be pure air whatever the composition of pure air is defined to be, not only because it is impractical if not impossible to attain

such a goal but also because 'pure air' might actually be more damaging than some contaminated air. One might justifiably say that ever since fire was invented, except for the occasional yogi who fasts and meditates for twelve years atop the Himalayas, no member of the homo-sapien-sapien race has ever breathed clean unpolluted air.

A more liberal attitude has been taken by ASTM in their designation (D 2356-67a): "Air pollution is constituted by presence of unwanted material in the air." One can logically conclude that the term "unwanted material" refers to material that exists in sufficient concentration for a sufficient time to interfere significantly with the comfort, health or welfare of persons or the full use and enjoyment of property. Indeed this view is reflected in the world health organization (WHO) definition, "Air pollution occurs when one or several air pollutants are present in such amounts and for such a long period in the outside air that they are harmful to humans, animals, plants or property, contribute to damage or may impair the well being or use of property to a measureable degree."

In a recent lecture on pollution, West[529] attempted to clarify the situation regarding terminology. He advocated the use of the non-derogatory word 'contaminant' to refer to whatever alters the pristine state of the environment and the word pollutant to be a contaminant present in sufficient concentration to adversely affect something that man values.

At this point, it is interesting to investigate the

etymological origin of the word 'pollution'. In middle english it was spelled with one l and originated from the past participle of the latin word polluere, in which pol is a prefix meaning 'for' and luere meaning to unleash something harmful. Even from historical perspective then, the term pollutants should be reserved for actually harmful or otherwise disagreeable contaminants.

It must be pointed out that, contrary to popular belief, official measures to control air pollution, including governmental legislations are not at all of recent origin. Even in medieval London malodorous trades were banished to the periphery of the town, and regulations against burning certain types of coal were quite strictly imposed. The first official legislation was the 'Alcali Act' of England in 1864, in connection with the control of hydrogen chloride and hydrogen sulfide emitted by LeBlanc soda plants. Since that time industrial output of all kinds has risen exponentially and concommitantly, so has pollution. Major disastrous episodes of air pollution have occurred a number of times, and are often cited. It is instructive to note that very few of these events have been caused by a brief accidental discharge but rather have resulted from adverse meterological conditions that led to slow accumulation of industrial emissions. The danger was always there, imminent, and it was characteristic of human nature to respond primarily to the dramatic and overlook the insidious. In the light of cold scientific observation, the damage due to pollution is very much like the tip of an iceberg. The greater part of the problem remains imperceptible, but becomes

apparent slowly and surely, and with the intense restiveness inherent to our civilization, is often difficult if not impossible to correlate in terms of a simple cause and effect relationship.

While detailed philosophy and legal aspects of air pollution control are far beyond the scope of this dissertation, details pertaining to pollutant species of our interest will be discussed in a later chapter. Suffice it to say that long before large scale attempts were made to prevent pollution of ambient air, working conditions at individual worksites in highly industrialized nations have been a subject of study to prevent health hazards to the worker. The study of health hazards in sulfuric acid plant environments began well over half a century ago. The chemist's task in such situations is to develop analytical methods to determine the pollutant of interest selectively and accurately and to provide such data to the occupational hygienist for evaluation.

Particulate Matter in the Air

Air pollutants may be broadly classified into gaseous and particulate matter. An alternative classification is primary and secondary pollutants; primary pollutants result from direct emission and secondary pollutants are reaction products of primary pollutants with other material, including themselves. While both gaseous and particulate air contaminants are largely of direct origin, a very substantial portion of airborne particulate matter that can definitely be termed pollutants does not result from direct emission. More than 90% of the particulate burden of the air however, is natural in origin[416] and relatively harmless

(pollens being a notable exception) both from a standpoint of chemical toxicity and more importantly from a standpoint of size. Particles of natural origin are usually too big to penetrate as far down as the lungs. Their sources are sea spray, volcanoes, meteors, forest fires, and natural wind erosion and grinding that lead to dust storms. Man-made particulates originate almost entirely from combustion processes (> 70% and the bulk of this from the combustion of coal) and other industrial operations. Although man-made particulates do not contribute significantly to the total particulate burden, they are inherently more dangerous because of their much smaller size and consequent ability to produce respiratory afflictions. Since 80% of the total atmospheric particulate burden is within 1 km from the ground, it is clear that any problem relating to airborne particulate matter is a local rather than a global effect.

The studies of Robinson,[416] a leading worker in this field, reveal that while indeed man-made sources contribute no more than 10% to the total particulate burden (amounting to 3×10^9 Mtons/yr), virtually all of the man-made burden is emitted within the latitude band 30°-60° North. As a result, the contribution of man-made sources to the total is much higher within this region, about 31%. This region alone is responsible for the much higher contribution of the northern hemisphere (17%) to the total, as compared to the global

average. In contrast, man-made sources account for no more than 1% of the total particulate burden in the southern hemisphere.

An examination of the energy consumption data (1968) reveals that the generation of particulates is well correlated with the consumption of energy. 96% of total global energy consumption occurs in the northern hemisphere and again 86% of the total is consumed within the latitude band 30^{o}-60^{o} North. A study of the U.S. alone corroborates the above conclusion. In 1968, the U.S. consumed 34% of the total consumption of the northern hemisphere and was responsible for 31% of the man-made atmospheric particulates in this hemisphere.

It was stated earlier that, in general, man-made particulate matter is considerably smaller in size than natural particulates. (The term used in sizing particulate matter is mass median diameter, MMD. In all discussions that follow the words particulate size and MMD will be used interchangeably). As a result of this smaller size their lifetime in the atmosphere is longer than that of naturally occurring particulates. Existing data indicate that the equilibrium fine particle concentration in the atmosphere is steadily increasing, primarily as a result of human activities. Generally, electrical conductivity is taken to be an inverse measure of fine particle concentration

because the fine particles act as efficient scavengers for the small ions, which in turn predominantly govern the electrical conductivity. The main advantage of atmospheric conductivity measurements is that it is little affected by the larger, naturally occuring particles. Cobb and Wells[104] have presented data on electrical conductivity measurements in the North Atlantic and the South Pacific regions; the data covers the period 1907-1967. Their results indicate that the conductivity has decreased in the North Atlantic region by at least 20% in the past 60 years, and beyond doubt, a 15% decrease has occurred since 1929. The authors conclude that this change in conductivity is equivalent to a doubling of the fine particle concentration in that region. In contrast, electrical conductivity measurements have shown no significant change during the past 60 years in the South Pacific region. Gunn[187] came to similar conclusions and stated further that the fine particle burden in the North Atlantic region definitely originates from the North American continent. Since no significant increase has been observed in the southern hemisphere one can conclude that a truly global increase has not occurred and the state of affairs represents some sort of a steady state in which the fine particle concentration only increased in the regions close to the emission sources. In this context, data from the North Pacific region would have been very valuable but are not available.

Flowers,[157] McCormick and Ludwig[307] have pointed out a similar increase in fine particle concentration in the 30^{o}-60^{o} North

latitude zone on the basis of atmospheric turbidity measurements; turbidity is also primarily governed by fine particles. Again, lack of any such increase over an extended period of time in the southern hemisphere is evident from analysis of the data presented by Fischer.[153]

These observations confirm that there has been a definite increase in fine particle concentration in regions where large quantities of energy are consumed and also that such increases are local and not global.

Particulate Sizing and Aerosols

In his classic text on air chemistry, Junge[248] introduced a classification of particulate matter that is based on size; with certain modifications this classification is generally used today. Particles with MMD between .001- .1 μm are called Aitken particles, after the name of John Aitken who first called attention to the formation of fog over urban areas after several hours of sunshine in the morning even though the temperature of the air and earth surface was increasing.[3] Particles with sizes between .1 - 1 μm are called Large particles and those larger than 1 μm in MMD are called Giant particles. Due to high rate of settling, particles much larger than 10 μm in size do not constitute a significant fraction of the total atmospheric burden. In terms of this classification (which will be used throughout the rest of this text) naturally generated particulate matter fall in the Giant particle class, and a substantial part of particulates from man-made sources fall in the Large particle class. Aitken nuclei are largely of terrestrial origin, the other important sources being automotive exhausts[512] and similar combustion sources. Aitken nuclei

are of paramount importance in weather processes because they serve as condensation nuclei for cloud formation.

The definition of aerosols is somewhat arbitrary. Possibly the best definition is that due to Hidy and Brock:[205] An aerosol is a suspension of particulate matter in the air, with small enough settling velocity such that they exhibit a certain degree of stability in a gravitational field.

In his treatise, the only existing text on the mechanics of aerosols available to date, the Russian scientist Fuchs[165] has given an elegant classification of aerosols. Dispersion aerosols are formed as a result of direct physical disintegration of solid and liquid matter whereas condensation aerosols are formed when supersaturated vapors condense and when gases react homogeneously to form a non-volatile product. In everyday terminology, any type of liquid aerosol whether it is a condensation or a dispersion aerosol is called mist, a dispersion aerosol in which a solid is dispersed is called dust, and a condensation aerosol in which a solid is dispersed is called smoke. One characteristic difference between solid and liquid aerosols that is immediately noticeable is the particle shape. Liquid aerosols are spherical (cf. microscopic determinations of aerosol sulfuric acid, Chapter V) but solid aerosols, in general, have completely variable and highly irregular particle shapes. Very often an actual aerosol mass is neither purely a dispersion nor a condensation aerosol but a mixture. When this mixture is one that results from a dispersed phase, usually solid, serving as a heterogeneous reaction site at which a growth of soluble matter in solution occurs (cf. catalytic

oxidation of SO_2 in the atmosphere, Chapter II), such a mixture is commonly called smog.

Chemical Composition of the Tropospheric Aerosol Mass

Firstly, the tropospheric aerosol mass can be divided into two distinct classes, continental and maritime. The maritime aerosol mass originates directly from the ocean and as such bears close resemblance to the solute composition of the ocean. Over coastal areas a mixture of continental and maritime aerosols exists while further inland almost purely continental aerosols are found. The difference between continental and maritime aerosols is often easy to determine without chemical analysis. While the peak concentration of particulate matter in a maritime aerosol occurs in the size fraction around 1 μm MMD, the peak concentration of particulate matter in a continental aerosol mass occurs in a size fraction almost an order of magnitude lower in MMD.

Very little is known about the chemical composition of the particles in the Aitken range, because a) collection is difficult and b) although they are present in very large numbers, the total mass is not substantial.

Among other things, Junge[248] initiated the study of total chemical composition of the tropospheric aerosol mass. The most surprising result that came out of these studies is that in the large particle class, sulfate constitutes overwhelmingly the burden of the aerosol mass. Sulfate is present, in general, in amounts almost two orders of magnitude greater than chloride or nitrate. These studies refer to background, that is non-urban regions of the northern hemisphere.

Typical compositions of these background aerosols are (in $\mu g/m^3$): Cl^-, 0.03; Na^+, 0.02; NO_3^-, 0.06; $SO_4^=$, 4.6; NH_4^+, 0.8. The mole ratio of NH_4^+ to $SO_4^=$ suggests a composition of $(NH_4)_2SO_4$.

Sulfates also constitute a substantial amount of the Giant particle burden although in this case other salts are present in comparable amounts.

These conclusions have been confirmed over and over by later studies.[499] On extension of these studies to highly industrialized urban regions it was found that sulfate is found in far larger excess than ammonium or other cations with which it is likely to be associated, thus necessitating the postulate of existence of acid sulfate species. Novakov's data[383] from Pasadena, for example, shows a preponderance of S(VI) i.e., sulfate over common cationic species. His data also indicates a substantial concentration of S(IV) species but since his technique of measurement (ESCA) is essentially a surface technique, it is an open question whether it is actually a sulfite species or is absorbed SO_2 on particulate matter.

Presently, it is generally believed that the sulfates (primarily $(NH_4)_2SO_4$ and NH_4HSO_4) are the end products of natural and man-made H_2S and SO_2. Not only do they dominate the tropospheric aerosol mass but they also constitute a significant portion of the stratospheric aerosol burden, the other part being meteoric dust. There seems to be little doubt[421] that the ammonium sulfates in the stratosphere originate from the troposphere, and being relatively volatile compared with other particulate matter, they migrate upward and once past the tropopause are protected from rapid washout by rain.

Extensive studies have been made on photochemical formation of aerosols in simulated urban atmospheres. A discussion of the photochemical and other mechanisms of oxidation of sulfur dioxide to sulfate will be deferred until a later chapter. Suffice to say that in a number of studies, typified by that of Groblicki and Nebel,[186] irradiation of trace mixtures of sulfur dioxide - nitric oxide - ozone and various hydrocarbons always resulted in the formation of aerosols in which the dominant component was ammonium sulfate.

Size Distribution, Sulfate Aerosol, and Factors Affecting the Distribution

The full extent of the mathematical details involved in a description of aerosol size distribution is beyond the scope of this dissertation. The simplest form is a power law due to Junge[248] which states

$$n(r) = \frac{dN}{d(\log r)} \quad cm^{-3} = C\, r^{-\beta}$$

N is the total number of particles with radii less than or equal to r, and n(r) is the number of particles between r and r + δr. The first part is rigorously valid; the second equation is an approximation. β has a value of about 3 and C is a constant only at a particular location, C generally increases with increasing degree of urbanization.[395]

Currently the log normal distribution function involving both the geometric mean size and the geometric standard deviation is generally regarded to be the most nearly valid;[80] however, the mathematical description is exceedingly complex.

The factors that affect that total number of aerosol particles

within a given size range were originally listed by Junge.[248] The following list is somewhat modified, as a result of our enhanced knowledge of atmospheric chemistry.

1. Production of particles from natural sources as mentioned previously.
2. Production of particles by combustion processes and by homogeneous gas phase reactions or heterogeneous nucleation processes, surface reactions, droplet reactions and subsequent evaporation, etc. (cf. secondary pollutants)
3. Growth of particles due to homogeneous gas phase reactions and attachment to a nucleation site, and due to direct heterogeneous reactions on particle surfaces.
4. Net change that results from thermal coagulation of smaller particles.
5. Net change that results from the mechanical destruction of large particles or from a phase change that causes dispersion of a condensed phase.[391]
6. Loss of particles through gravitational sedimentation, effects of turbulent velocity gradients and scavenging of smaller particles by larger ones during their fall.
7. Loss of particles as a result of impaction on obstacles in their trajectory.
8. Loss of particles by washout during precipitation, (rain, snow, sleet, etc.)

It is obvious that processes 2 and 3 are the only ones directly affected by human activities. The rate of coagulation is proportional

to the total number of particles, but the coagulation does not alter the total quantity of material present. This process is of paramount importance for Aitken particles whereas the last three processes are very effective in removing giant particles from the atmosphere.

It has been suggested by Friedlander and Wang[160] that eventually a coagulating aerosol will reach a steady state size distribution, which has the same form regardless of the initial size distribution. The final state usually has a distribution that contains many large particles and may be termed to have the self preserving size distribution. In this steady state, gains in the number of particles in a given size fraction are balanced by losses.

Like most other man-made particulate matter the sulfate aerosol mass has a peak concentration in the large particle fraction. Through laboratory studies Gillespie and Johnstone[177] indicated that sulfate aerosols formed by means of photooxidation of sulfur dioxide are generally within the 0.2 - 0.45 μ size range. For a given experimental run, these sulfate aerosols are remarkably size-homogeneous with a geometric standard deviation of only 1.1 - 1.3. Of numerous ambient studies reported the studies carried out by Roesler, et al.[420] in Chicago and Cincinnati are noteworthy. These workers found the sulfate ion to account for at least 20% of the total aerosol burden in the atmospheres of these highly industrialized cities and estimated on the basis of a cyclone separation stage that about 90% of the sulfate aerosol was capable of direct penetration into the lungs.

There exists a fortuitious circumstance in regard to the long

range transport of sulfate aerosols. Although the rate of formation of sulfate aerosols increases rapidly with increasing humidity, the aerosols are removed very efficiently by the subsequent rain.[461]

There is very little available data on the actual size distribution of free sulfuric acid aerosol in ambient air. Since sulfuric acid is highly hygroscopic it is expected that such distribution would be governed by the prevailing relative humidity.[173] In this context, Junge and Scheich's[249] data, obtained by measurements made at urban European locations is very interesting. They report that not only is the free acidity almost exclusively associated with particles in the Aitken region, so is the bulk of other soluble matter. Therefore, it seems probable that the size distribution of sulfate aerosols in urban areas and non-urban regions are actually quite different. Johnstone[243] points out that sulfate aerosols formed by catalytic rather than photochemical oxidation of SO_2 should have a size that depends strictly on the heterogeneous reaction site and may be anywhere between 0.1 - 10 μ. In a later chapter the various mechanisms leading to the formation of aerosol sulfates will be discussed; it is indeed possible that the observed difference in size distribution in different instances results from altogether different mechanisms of formation. If Junge and Sceich's data are valid, the problem becomes a much more severe one because particles smaller than 0.1 μm in diameter are not removed effectively by weather processes.

Mobility and Transport of Aerosols

Since virtually the whole text of Fuchs[165] is devoted to the extremely complex subject of aerosol mobility and transport, the

interested reader is referred to this source. Some aspects of the magnitude of such a complex problem have been discussed elegantly by Peskin.[383]

If B is the mobility (the ratio of the velocity to the force imposed on it) of a particle with a radius r, then as a crude approximation B is inversely proportional to r. This approximation is reasonable only in the case of steady rectilinear motion.

For our purposes, it is important to understand qualitatively that in the absence of specific removal processes such as rainfall, a locally built up concentration of aerosols would reduce by diffusion slower than that in an otherwise identical system involving gaseous contaminants that had the same concentration gradient.

The problem of building up high local concentrations of contaminants in the aerosol form therefore is potentially much more acute than with gaseous contaminants. Furthermore, increasing the height of exhaust stacks to combat the problem is not as effective a solution in this case as with purely gaseous pollutants because the bulk of the aerosol burden will pass through the breathing zone before eventually settling out.

Aerosols and Visibility

Since visibility is the index of air contamination to the layman, it is worthwhile to investigate the relationship between visibility and total aerosol loading.

The following definition of visibility is given in the Glossary of Meterology.[223]

"... The greatest distance in a given direction at which it is

just possible to see and identify with the unaided eye (a) in the daytime, a prominent dark object against the sky at the horizon and (b) at night, a known preferably unfocused moderately intense light source."

Beer's law is applicable to visibility studies, but must be modified so that the extinction ooefficient in this case is the sum of the absorption and scattering coefficients.

Of the different forms of scattering, Rayleigh scattering is relatively unimportant in affecting visibility in aerosol loaded air, because the extent of Rayleigh scattering is significant only for particles much smaller in size than the wavelength of the incident light. When the wavelength of the incident light is comparable to the particle size the dominant form of scattering is Mie scattering that is named after the man who developed the theoretical foundation for such phenomena. Mie scattering, in conjunction with the absorptive attenuation, is the dominant factor in governing visibility in a contaminated air mass.[412] Particles in the large class (0.1 - 1 μ), therefore appear to be the ones most effective in reducing visibility.

Charlson[93] has produced an empirical but useful correlation between total aerosol loading and visibility which states that visibility in km = 1800/total aerosol loading in mg/m^3.

Lundgren's[299] study suggests that inorganic material (sulfates and possibly nitrates) is largely responsible for reduced visibility during photochemical smog episodes. There are some other facts that have been established by laboratory studies:[148,195] a) Very very few hydrocarbons will form aerosols when irradiated with NO_2 alone;

b) almost all hydrocarbons form aerosols upon irradiation when NO_2 and SO_2 are both present; c) when SO_2 is present the aerosol will invariably be dominated by sulfate, to the extent that the aerosol may not even contain any carbon compounds.

The above points substantiate the paramountly important role that sulfate aerosols play in atmospheric processes. But what has happened to visibility during the course of years? While no apparent overall change in visibility was reported[64] over London during the period 1950-1959, visibility over the California central valley reportedly underwent a steady decrease for 20 years up to 1960.[211] The most thorough study is that due to Holzworth[212] who accumulated data at 28 different locations in the U.S. over a long period of time.

According to this study, although a steady worsening was observed at most locations up to a certain period, in almost all cases visibility is better today than it was 15 - 20 years ago, because of the more stringent emission controls and better control measures.

The very impressive improvements in air quality in general and visibility in particular in cities such as St. Louis and Chicago over the past two decades instill some optimism, hopefully with the advent of better and judiciously applied control measures a better future lies ahead.

CHAPTER II

THE SULFUR CYCLE AND THE PATHWAYS TO AIRBORNE SULFATE

"As soon as I had escaped the heavy air of Rome and the stench of its smoky chimneys, which when stirred, poured forth whatever pestilent vapors and soot they held enclosed, I felt a change in my disposition."

- Seneca, 1st. Century A.D.

In view of the finiteness of our atmosphere, it becomes important to review the knowledge of the sources of and sinks for sulfur compounds, since beyond a doubt, they are the single most important class of compounds in the general study of ambient air pollution. One can then take a step further forward and evaluate the nature of the added burden that man is putting into the air that surrounds him.

An excellent and reasonably recent article on the sulfur cycle by Kellogg et al.[254] is available. Other equally good sources of information, albeit older ones, by Robinson and Robbins[413,414] exist and provide valuable data and insight. A massive amount of data is available in an EPA Publication,[91] which is invaluable in evaluating the total man contributed sulfur burden of the atmosphere.

The Sulfur Cycle

In the main, sulfur is released to the atmosphere in three primary contaminant forms. These forms are hydrogen sulfude, sulfur dioxide, and sulfate from sea-spray. The sulfate content of sea-spray is mostly sodium sulfate along with traces of calcium and magnesium sulfates. Although it is an important fraction of maritime aerosol, sulfates from sea-spray has little to do with inland air pollution problems. Some elemental sulfur is emitted during volcanic emissions. However, over an extended time basis the sum total of sulfur compounds emitted by volcanoes is insignificant, although such emissions can drastically change stratospheric particle concentration and thus affect weather patterns severely for long periods.

Hydrogen Sulfide

The emission of hydrogen sulfide, natural and otherwise, is dominated by microbial processes. Hydrogen sulfide is possibly the only important natural pollutant that sometimes disturbs nature's own life processes. Generally, ambient air contamination due to H_2S is negligible as is the total industrial H_2S emission. Although the compound is dangerously toxic when its concentration exceeds a certain level, no evidence of cumulative toxicity exists and fortunately its extremely disagreeable odor is perceivable in concentrations far lower than dangerous levels. The total amount of H_2S released to the atmosphere* is somewhat controversial and is stated to be anywhere between ~ 90 million Mtons[254,413-4] to 270 million Mtons.[149,248] The high values are based on an estimate that attributes more than two-thirds of the emission to the oceans. This concept involves a total transfer of sulfur from the oceans to the land[414] and is unlikely because the solubility and reactivity of the gas would tend to favor its retention in the ocean.[374] The low figures were derived primarily from budgetary considerations. Kellogg et al[254] prefer to be conservatively uncertain in ascribing the percentage of this amount originating from the oceans. Robinson and Robbins[413-4] in their total figure of 100 million Mtons (reestimated in a later publication[415] to be 90 million Mtons).estimate only about 30% to be the oceanic

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*All emission figures in this cyapter, unless otherwise stated, will be quoted in terms of sulfur for budgetary simplicity.

contribution. It is generally agreed, however, that the oceanic emission is predominantly localized over the coastal regions rather than over the oceanic mass itself. In any case, even if the lower and more recent figures are taken to be valid, they still account for roughly half of the total sulfur released to the air.

It would be safe to say that the ambient background levels of hydrogen sulfide are not known with any certainty. They have been reported to be anywhere between part per trillion levels to several parts per billion levels.[248,292] It is significant that virtually all of these data are obtained by means of liquid scrubber sampling techniques which give completely unreliable results in the presence of SO_2, the omnipresent stepbrother of H_2S.[460] The best estimates of the background levels of H_2S place it around 0.2 ppb or about 0.3 $\mu g/m^3$.[512]*

All sulfur compounds emitted to the air finally end up in the most stable oxidation state, i.e., sulfate. The ultimate fate of H_2S is not different, but apparently the oxidation of H_2S proceeds via the formation of SO_2. Since the mechanisms involving the oxidation of SO_2 to sulfate will be discussed later in some detail, it will suffice here to look into the possible pathways for oxidation of H_2S to SO_2. A very small amount of H_2S may be consumed directly by certain photosynthetic processes.

Theoretically, H_2S can react photochemically with molecular oxygen. The principal energy absorption of the compound however,

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*From this point on all air contaminant concentrations will be expressed in terms of $\mu g/m^3$ at 20^oC. Simple conversion factors to ppm and viceversa have been tabulated by Leithe.[278]

lies well below 290 nm and since these wavelengths do not penetrate the troposphere, it is unlikely that such processes are significant in the lower atmosphere. On the other hand, it is quite likely that this photochemical process is dominant in the conversion of stratospheric hydrogen sulfide into sulfate. It is possible that the direct oxidation by oxygen is much more rapid when both reactants are in the form of droplet solutions.

Oxidation by atomic oxygen should be fast and should proceed via a radical chain growth mechanism. This pathway is unlikely to be important except in severely polluted atmospheres in which NO_2 and O_3, from both of which atomic oxygen is produced in significant quantities by photolysis, are simultaneously present.

The dominant mode of H_2S oxidation appears to be heterogeneous surface reactions with ozone. Originally observed by Robbins,[409] the oxidation of H_2S by ozone on particle surfaces that leads to the production of water and SO_2, was confirmed by Cadle and Ledford[83] to be extremely rapid. The rate of oxidation is independent of H_2S concentration and is dependent largely on the available surface area. Other factors remaining constant, the reaction is 1.5 order with respect to ozone. The reported rate constant and the observed ambient levels of particulate matter and ozone present in the air has been used to calculate the residence time of H_2S in our atmosphere. The residence time is not more than two days and in highly contaminated systems, may be as small as two hours.[413]

In a sense this removal process implies that atmospheric

reactions are generally interrelated and thus efforts to remove a specific contaminant from the atmosphere may not always produce desired results. If, for example, the ambient concentration of ozone could be drastically reduced to a level that would satisfy some extreme "environmentalists", it is likely that there would be a malodorous world.

Sulfur Dioxide

Sulfur dioxide remains the principal primary contaminant that results from human activities. Apart from volcanic emissions which contribute minor quantities of SO_2, there are no known natural sources of SO_2 that contribute significantly to the total emission. The latest available estimates (for 1970) indicate a worldwide total emission figure of 67 million Mtons of which roughly 90% or 60 million Mtons are emitted in the northern hemisphere.[415] There is a direct correlation between energy consumption and SO_2 emissions. The U.S. accounted for $\sim 34\%$ of the total energy consumed in the northern hemispheres and was responsible for $\sim 30\%$ of the total SO_2 emission in this hemisphere.[416]

Approximately a third of the total sulfur released to the atmosphere is in the form of SO_2 and is entirely man made. Because this emission is further localized in urban or peripheral urban areas, it is no wonder that SO_2 can and does cause severe air pollution problems when meterological conditions are adverse.

An itemization of SO_2 emissions from different sources will be presented in Chapter VI.

Budget Balancing

The ultimate fate of SO_2, whether it is a primary pollutant or the result of the oxidation of H_2S, is its conversion to sulfate. Only a trivial amount is consumed directly by plants. As stated earlier, regardless of the oxidation state in which sulfur is released into the atmosphere, it will eventually become sulfate. The mass balance of sulfur emission is completed by sulfate from sea-spray, estimated to amount to 43 million Mtons of sulfur.[149] Approximately 90% of this quantity, however, is precipitated over the mid oceans, and only 10% influences the coastal aerosol compositions. Such maritime aerosols thus contribute little or nothing to inland aerosol compositions. Because sulfur dioxide emissions are essentially confined to land masses, the data presented in this chapter can be used to demonstrate that over the land masses man made sulfur emissions in the form of SO_2 amounts to 50% of the total sulfur emissions. This estimate can be confirmed by the available isotopic data;[234,323] the basis for such proof is the different isotopic ratios in biogenic and fossil fuel sulfur. The study of ice in glaciers has shown that in spite of the increasing sulfur oxide emissions, the atmospheric background levels of SO_2 have not increased[83] and are estimated to be around 0.2 ppb or 0.5 $\mu g/m^3$. Most investigators believe that the environmental sulfur cycle is virtually 100% balanced. Presently, the steady-state total amount of sulfur in the atmosphere is estimated to be 100 million Mtons, whereas the total oceanic sulfur content is a staggering 1000 trillion Mtons. Thus, the

oceans are by far the largest sinks for sulfur. Of the ~200 million Mtons of sulfur released annually (45% as H_2S, 34% as SO_2, 21% as sulfate from sea spray) ~5% is dry deposited on land surfaces, ~8% is directly consumed by plants, ~47% is removed from the air by precipitation over the land masses and the other 40% is similarly removed by precipitation over the oceans. It is obvious that a net land to sea mass transfer occurs because much of the sulfates washed onto the land areas is also carried to the sea by rivers. In view of the enormous sink capacity of the oceans, no significant change in oceanic composition is expected.

The Pathways to Airborne Sulfate

There are three sources of aerosol sulfate in ambient air. The first is sulfate from sea spray, which as stated before, is not very important; the second and the main source is the oxidation of sulfur dioxide, and the third source is direct emission of sulfuric acid and/or SO_3. The total tonnage of the last item is not very significant either, and this emission is not a problem except in certain specific areas.

The Conversion of Sulfur Dioxide into Sulfate

It is doubtful if any other environmentally important reaction has been studied in greater detail than has the conversion of SO_2 into sulfate. As a result, a huge body of scientific literature about the subject has accumulated, and much of it is controversial. Several possible and probable reaction modes have been established.

A number of excellent review articles are available[8,84,253,456,509] in the recent literature, the reviewers do not agree on the dominant mechanism responsible for the atmospheric conversion of SO_2 to sulfate. Indeed it is likely that there is no generally dominant pathway but rather the course is governed by the existing environmental conditions.

Virtually all of the early work done on the subject was carried out by H. F. Johnstone and his co-workers, first at Ohio State University and later at the University of Illinois at Urbana. Johnstone was apparently the first person to realize that there is a possibility of relatively harmless levels of SO_2 undergoing rapid oxidation to dangerous levels of aerosol sulfuric acid. It was empirically taken for granted for a long time that sulfur trioxide formed as an intermediate is almost immediately converted to sulfuric acid as long as there is a measurable humidity. Recently measured rate and equilibrium data[200] confirm this conclusion.

The two basic mechanisms investigated by Johnstone were photochemical and catalytic, and all the later refinements can still be classified under these two broad categories.

Photooxidation of Sulfur Dioxide

On the basis of their pioneering investigations, Gerhard and Johnstone[173] suggested that the rate of photooxidation of SO_2 to SO_3 and hence to H_2SO_4 in sunlight was less than 0.2% per hour and was not affected by the presence of NaCl, NO_2 or changes in relative humidity (R.H.) within the range of 30-90%. Although

substantially higher rates of H_2SO_4 aerosol formation was reported later by Renzetti and Doyle,[401] recent studies by Junge[248] do not confirm these conclusions and suggest a much lower rate, close to that proposed by Gerhard and Johnstone.

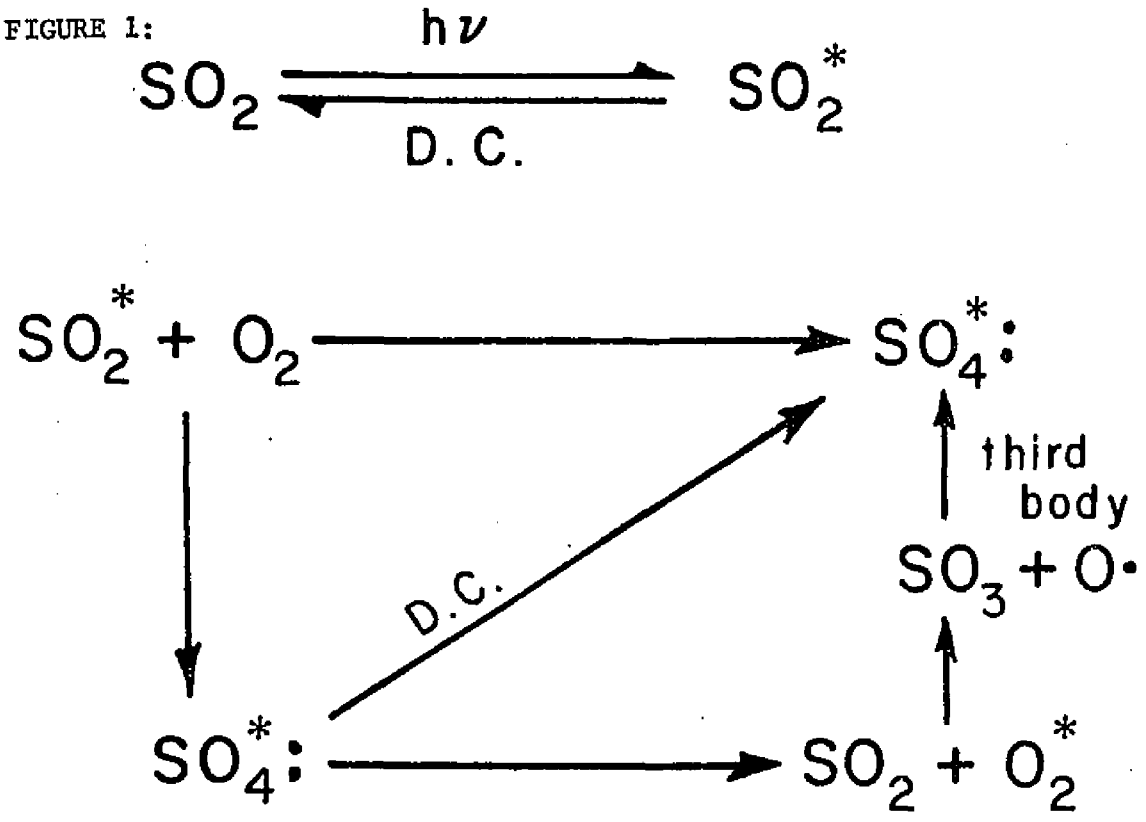
While the bond dissociation energy of the SO_2 molecule is far too high to permit photochemical generation of the :SO species, at least five different excited states (three triplets and two singlets) of SO_2 have been established, all to be generated by readily available solar radiation.[200]

The generally postulated mechanism involves the SO_4 biradical as an intermediate. Within the scope of this brief survey it is impossible to examine in detail the multitude of proposed mechanisms. A group of the postulated reactions[8,61,84,116,192,253,456,466,490,509] is summarized in Fig. 1.

It is important to note that not a single one of the proposed photooxidation mechanisms proposed is sufficiently fast (with the possible exception of the mechanism postulated by Sidebottom, et al.[456] who reported a maximum possible SO_2 disappearance of 2% per hour) to account for the relatively fast rate of removal of SO_2 from the atmosphere that is observed. A mathematical model for the kinetics of direct photo oxidation processes has been presented by Takahashi et al.[474] and the latest experimental data on direct oxidation of SO_2 in otherwise uncontaminated air are available from the work of Clark and Whitby.[102] The observed rate never exceeded 1% per hour.

The actual operative mechanism may be a photochemical one

FIGURE 1:



$$SO_4: + SO_2 \rightarrow 2\,SO_3$$

$$SO_4: + O_2 \rightarrow SO_3 + O_3$$

$$O_3 \underset{\text{Third body}}{\overset{h\nu}{\rightleftharpoons}} O_2 + O\cdot$$

$$SO_2 + O \underset{h\nu}{\overset{\text{Third body}}{\rightleftharpoons}} SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

D.C. = Deactivation by Collisions etc.

that is complicated by the presence of other contaminants in the air. Although photolysis of SO_2 with hydrocarbons has been shown to produce sulfinic acids (RSO_2H)[116] and sulfonic acids (RSO_3H)[238,369] via a free radical mechanism, this path is not generally regarded to be an important route for removing atmospheric SO_2. The situation however, is quite different when mixtures of SO_2, hydrocarbons, and oxides of nitrogen are irradiated. Sulfur dioxide is consumed at a rapid rate upon irradiation of such mixtures[148,286,400,406,444,445,508] and highly acid sulfate dominant aerosols always result. There are some important aspects of such reactions:

a) When there is no SO_2 little or no aerosol formation is observed.

b) Saturated hydrocarbons are far less reactive than unsaturated ones.

c) When a mixture of unsaturated hydrocarbons and SO_2 is irradiated, the presence of NO_2 is generally necessary for SO_2 to be oxidized. When there is no NO_2 present, an olefin may even retard the SO_2 photooxidation rate.[401]

d) Both the oxidation of NO to NO_2 and the formation of peroxyacetylnitrites (PAN) are inhibited by SO_2.[532-3]

e) The rapid conversion of SO_2 to sulfuric acid in these systems has been shown to occur at ambient concentrations.[444] Unlike most other systems studied, no extrapolation from higher concentrations to ambient concentration levels is necessary in these systems.

The exact reaction mechanisms in these systems are uncertain primarily because some very difficultly measurable rate data for certain free radical reactions are unavailable. According to Calvert, et al.[86] the reaction mechanism probably involves the alkylperoxy radical RO_2.

$$R\cdot + O_2 \xrightarrow[\text{Third body}]{} RO_2\cdot$$

$$RO_2\cdot + SO_2 \longrightarrow RO\cdot + SO_3$$

This mechanism could be operative in photochemical smog in which relatively high free radical concentrations are known to exist. The first reaction has been independently estimated to be very rapid.

It is possible that the catalytic action of NO_2 plays a part through the formation of nitrosylsulfuric acid (cf. the chamber process for sulfuric acid production) but in view of the very low ambient concentrations of NO_x encountered, such a process is unlikely to make any substantial contribution.

Very similar to the hydrocarbon - NO_x - SO_2 systems, olefin - O_3 - SO_2 systems show a rapid conversion of SO_2 to sulfuric acid[195] primarily by means of a similar mechanism involving alkylperoxy radicals. The reaction of SO_2 with ozone by itself is too slow to be important. Payne[378] has pointed out that in analogy with oxidations by alkoxy and alkylperoxy radicals, reactions with hydroxy and hydroperoxy ($HO\cdot$ and $HO_2\cdot$) radicals may also take place. The measured rate constants, however, are very much lower than corresponding values obtained for hydrocarbon - NO_x - SO_2 systems

in which the alkoxy and alkylperoxy radicals are postulated to be involved. Such mechanisms therefore are also unlikely to be significant.

Catalytic Processes

a. Heterogeneous Oxidation:

Oxidation of SO_2 to sulfate may occur on dry particle surfaces, but there is no evidence to indicate that inert particles such as silica or sodium chloride provide useful reaction sites. An insignificant portion of atmospheric SO_2 may be removed via physical adsorption on inert particles and subsequent removal by rainfall or snowfall.[536] Alkaline particulates such as calcium carbonate may be effective in oxidation by providing a chemisorption step that precedes the oxidation. Practically no data are available to indicate to what extent these mechanisms may be operative in converting SO_2 to sulfate in the ambient atmosphere.

b. Homogeneous Aqueous Phase Oxidation:

Many authors believe that the bulk of the atmospheric SO_2 in contaminated atmospheres is removed by oxidation in solution droplets. When SO_2 is dissolved in water droplets, sulfite ion formation occurs as a result of consecutive equilibria involving sulfurous acid and the bisulfite ion. The sulfite ion can be oxidized by oxygen to form sulfate. The rate limiting process is the oxidation itself rather than the diffusion controlled dissolution of SO_2 and oxygen in the droplet. The process thus might be considered to be homogeneous. In the absence of catalytic agents, the reaction rate is not fast enough to account for the

observed observed rates of removal of SO_2 from the atmosphere. A detailed study of the mechanism and the reaction rates involved in the absence of catalytic agents has been given by Miller and dePena;[340] interpretation of data reported by previous workers is also included in this report.

In the presence of contaminants such as transition metal ions, the reaction rate is increased. In particular, manganese and iron salts have drastic effects.[241-2,247] Studies in this laboratory show that several other transition metal ions may also be highly effective in promoting such oxidation.[308] The mechanism involved in such processes was originally envisioned to be the one that follows.[331]

$$SO_2 + M(H_2O)_x^{2+} \rightleftharpoons (H_2O)_{x-1}M{\cdot}SO_2^{2+} + H_2O$$

$$(H_2O)_{x-1}M{\cdot}SO_2^{2+} + \tfrac{1}{2}O_2 \rightleftharpoons (H_2O)_{x-1}M{\cdot}SO_3^{2+}$$

$$(H_2O)_{x-1}M{\cdot}SO_3^{2+} + 2H_2O \longrightarrow M(H_2O)_x^{2+} + H^+ + HSO_4^-$$

The problem with such a scheme is twofold: it does not readily account for the generally observed decrease in reaction rate with time (or better, decrease in reaction rate with decreasing pH) and it requires unreasonably high concentrations of metal ions for the reaction to proceed at a reasonable rate.

The exact path of these reactions is not clear. Junge and Ryan[247] observed a considerably lower rate of oxidation when the reactions were carried out in the dark; this observation indicates that photolysis may also be involved simultaneously. Recently

flash photolysis studies have indicated that the following mechanism may be operative.[466]

$$SO_3^{2-} \xrightarrow{h\upsilon} SO_3^- + e^-(aq)$$

$$SO_3^- + O_2 \longrightarrow SO_5^-$$

$$SO_5^- + SO_3^{2-} \longrightarrow SO_4^- + SO_4^{2-}$$

$$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^-$$

$$SO_5^- + SO_5^- \longrightarrow SO_4^{=} + \text{Products}$$

$$SO_4^- + SO_4^- \longrightarrow SO_4^{=} + \text{Products}$$

The first step, leading to the formation of the SO_3^- species, is believed to be rate determining and may take an alternative route in the presence of certain transition metal ions, M^{+n}:

$$SO_3^{2-} + M^{+n} \longrightarrow SO_3^- + M^{+(n-1)}$$

The $M^{+(n-1)}$ species is postulated to be stabilized by complexation with sulfite. Whether the reduction of the metal ion by sulfite is catalyzed by light is unknown.

For continued oxidation to occur in such a system, the equilibrium concentration of the sulfite ion must be maintained at a reasonable level, i.e., the pH in the droplet must not fall below a certain value. The most logical way to form such a buffered system is by the dissolution of atmospheric ammonia in the droplet.

An increase in pH due to dissolution of ammonia in the droplet leads to a higher SO_2 solubility and a higher equilibrium concentration of the sulfite ion. The oxidation of SO_2 to sulfate in such

a system is quite fast even in the absence of metal ions,[511] and some researchers believe that ammonium ion may actually be catalytically involved in the process.[162] The role of ammonia however, can hardly be called catalytic since it is consumed during the process. Healy, et al.[197] estimate that in high humidity levels this route alone could well account for the removal of atmospheric SO_2. However, one must yet note that the oxidation rate is substantially faster in the presence of certain metal ions.

The original work on the kinetics of a pure system (i.e., not containing metal ions) was that of Scott and Hobbs.[447] The calculations are based on Henry's law equilibria involving SO_2, O_2, NH_3 as well as CO_2.

In conclusion, it is obvious that there is no generally applicable route by means of which SO_2 is converted into sulfate. The dominant route would be greatly dependent on the concentration of other contaminants, the intensity of sunlight, the humidity of the ambient air, etc. All of the various chemical species that may catalyze such a reaction are not known either. Particles of industrial fly ash have been shown to be excellent catalysts.[243] The importance of ambient humidity levels cannot be overstressed because humidity determines whether a soluble particulate with possible catalytic properties is present as a solid or a liquid aerosol.

The fact that the dominant route of conversion is dependent on various factors including diurnal variations has been demonstrated by Meszaros in a series of papers.[336] On the basis of studies

done in Budapest, Hungary, he concluded that the mechanism through which the formation of atmospheric sulfate particulates occurs cannot be the same in summer and winter.

Direct Emission of Sulfur Trioxide/Sulfuric Acid

Sulfur trioxide and H_2SO_4 are emitted from H_2SO_4 manufacturing plant stacks but these emissions are not generally regarded to be a problem of the ambient atmosphere because the particle size is large and relatively fast sedimentation rates are observed outside the stack. Needless to say, it is a problem inside the plant, and controls are necessary.

A problem of more general importance is that due to cars equipped with oxidative catalytic converters. Starting with the model year 1975, catalytic converters are being installed in gasoline operated automobiles sold in the United States. In the absence of a catalytic converter, the sulfur in gasoline is emitted as sulfur dioxide. A catalytic converter is an afterburner containing a noble metal catalyst. The purpose of the catalyst is to reduce the exhaust levels of hydrocarbons, CO and NO by oxidation. Unfortunately, the catalyst also oxidizes the SO_2 in the exhaust gases to SO_3 at the same time; such a catalytic process has been exploited in the chemical industry for a long time for the manufacture of sulfuric acid (cf. the contact process). The sulfur trioxide that is thus emitted into the ambient atmosphere is very quickly converted to sulfuric acid in the form of very fine liquid particulates.

The percentage of the sulfur in fuel that is oxidized to

sulfuric acid depends on various factors such as the type of engine, the operating rpm, the air/fuel ratio, the exhaust gas temperature, the space velocity, and most important of all, the exact type of catalyst. Conversion percentages in EPA sponsored studies have been given variously between 10-80% (Exxon, Ford, EPA, GM).[450]

The estimates of ambient levels of aerosol sulfuric acid which widespread use of catalytic converters may lead to in areas with heavy traffic density vary between 50 to 150 mg/m^3. In their own study, EPA scientists estimated a maximum concentration of 60 $\mu g/m^3$.

Pierson[386] has recently written an excellent article in which he has compiled most of the available data on the operation and emission characteristics of the catalytic converters that are now being used.

When there is no catalyst the concentrations of hydrogen and reducing hydrocarbons in the exhaust stream are overwhelmingly large relative to that of SO_2. The sulfate emission under these conditions is less than 1%[110] because reducing conditions exist and since such vehicles use leaded fuel, this emission probably occurs in the form of $PbSO_4$.

The salient points about exhaust gases from automobiles equipped with catalytic converters that appear in the currently available literature now follow.

a) Sulfuric acid is emitted from the tailpipe as a gas since the exhaust temperature is considerably greater than the dewpoint ($\sim 140^{\circ}C$).[285] Direct emission of SO_3 does not take place since

such a process is feasible only when exhaust temperatures are greater than 400°C.

b) The mass median diameter of the H_2SO_4 aerosol particles formed from the gas is in the Aitken range, i.e., less than 0.1μm.[110]

c) Virtually the entire particulate emission from a catalyst equipped vehicle is sulfuric acid and its associated water. Because of the hygroscopicity of the acid aerosol, the weight of particulate matter emitted/gallon of fuel is a term that has little meaning and depends on the humidity levels that exist during the measurement. A small amount of ammonium sulfate is also generally found and presumably results from reaction of the ammonia present in the exhaust gases with the sulfuric acid.[196]

d) Consideration of the various parameters that affect the conversion indicates that approximately 50% is the best estimate for the extent of oxidation of total fuel sulfur to sulfate.[385]

e) The emission rate is greatly dependent on the age and operating history of the catalyst. Alumina is generally used as a substrate, and although it does not store SO_2 to any significant degree, a substantial amount of SO_3 is stored as aluminum sulfate. As much as 3% conversion of the total amount of the catalyst substrate has been observed.[494] Finally a dynamic steady-state is attained between storage and release, the exact nature of the steady-state depends on the exhaust stream composition and the temperature.

f) The efficiency of SO_2 oxidation is dependent on catalyst age, but

the maximum possible extent depends upon the specific type of catalyst used as well as its operating history.

g) For some catalysts the steady-state between conversion and release is reached within normal limits of exhaust stream temperatures and transit times over the catalyst. For some catalysts the steady-state conditions are never achieved. In the latter case, the oxygen concentration has been shown to be the key factor in governing the conversion rates. The current hypothesis[338] is that the conversion rate is affected until the oxygen concentration is sufficient ($\sim 0.5\%$ of the exhaust stream) to cover all the active catalytic sites. Beyond this concentration increase in oxygen concentration has no effect on the oxidation rate.

h) Data obtained from the investigation of continuous operations cannot be extrapolated to explain cyclic operations. Cyclic operation is the realistic case. In general, such extrapolations provide values that are somewhat higher than the observed values.

What is the lifetime of free sulfuric acid thus emitted to the ambient air? If it is neutralized quickly, is it neutralized all the way to normal sufate or does it stop at an intermediate stage, i.e., bisulfate? The answer to any of these questions is not known. While the acid aerosol may react with particulates such as sodium chloride to form sodium sulfate/bisulfate and hydrochloric acid, logically one would expect neutralization by atmospheric ammonia to be the dominant mechanism for neutralization.

In the laboratory, attempts have been made to study the neutralization rates of artificially generated aerosol sulfuric acid by gaseous ammonia.[82,85,240,408] The reaction is diffusion controlled and apparently every collision is effective. Normally the reaction rate is too fast to be measured.

If these studies were directly applicable to the actual state of affairs in the ambient atmosphere and if one of the higher reported values of atmospheric ammonia concentration[186] is used, e.g., 100 $\mu g/m^3$, and if a mass median diameter of 0.1μm is assumed for sulfuric acid aerosol, a quick calculation would reveal that the residence time of free sulfuric acid would only be a few seconds and consequently there would be little chance of detecting the free acid in the atmosphere. Nevertheless, free sulfuric acid is routinely detected in our urban atmospheres. This detection alone led Lau and Charlson[269] to conclude that atmospheric ammonia concentrations must be substantially lower than those that had been reported.

Actually, there is no agreement between various measured values of the atmospheric ammonia concentrations. Some authors[124,342] report this concentration to be in the 10$\mu g/m^3$ range while Healy[198], who conducted a rather exhaustive study in the United Kingdom, reports that it is substantially lower. Junge, et al.[249] were the first to point out our inadequate knowledge of the ammonia concentrations.

While ammonia concentrations in the urban atmosphere may

indeed be very much lower than 10 $\mu g/m^3$, Junge and Scheich's hypothesis that the acid aerosol particles in the ambient atmosphere may be coated with unreactive films of hydrocarbons and other such organic material is an alternative possibility and should be investigated.

It is possible that both explanations have some merit. In a later chapter, the relative merits will be investigated.

CHAPTER III

HAZARDS POSED BY AIRBORNE SULFATE

"... Experience has indicated that it may take many years before the incidence of a disease is recognized as having a relation to exposure to a chemical."

- J. M. Barnes, The British Medical Journal, 1961

In the ambient atmosphere sulphur dioxide and airborne sulfate are so intimately related that it is usually impossible to attribute observed effects specifically to one or the other form.

The effect of a single species or that of a mixture that has a particular composition can be studied in the laboratory, but extrapolation of such data to the ambient atmosphere may not lead to meaningful conclusions.

Sulfur dioxide remains the single air contaminant for which the hazardous effects have been studied the most thoroughly and the damaging potentials have been best evaluated. As far back as 1954 the famous industrial hygienist Greenwald[184] pointed out that sulfuric acid and sulfates are constant companions whenever significant levels of sulfur dioxide are present. However, in surveying effects of ambient air pollution no attempts were made, except in very recent studies, to take into account the amounts of sulfuric acid and/or other aerosol sulfates that were present with the sulfur dioxide. In view of the general lack of knowledge of the amounts of airborne sulfuric acid and sulfates present along with SO_2 in these studies, the specific interpretation of the results obtained in the early studies is difficult, if not altogether impossible. This becomes specifically important because the hazards posed by sulfuric acid and ammonium sulfates are not less important than those posed by SO_2 and in combination the effect is more than additive.

However, it must be realized that the absence of this information is not as much due to oversight as one might be inclined to believe, but rather is due to difficulties in measuring airborne

sulfate and further, to determine the particular form of the sulfate.

Except for the purposes of comparison, no attempt therefore will be made to cover or refer to the great body of literature that reports the effects of SO_2.

Air pollution in general, has psychologic effects in addition to its physiologic threat and often deterioration of visibility has very heinous implications to the layman. The factors governing visibility have been discussed earlier, and it would not perhaps be repetitious to point out that atmospheric sulfates constitute a very large fraction of atmospheric aerosols that belong to the size class which primarily govern visibility.

Although extensive amounts of work have been done to establish the damage SO_2 does to certain types of vegetation, airborne sulfate has not been shown to cause agricultural problems. Sulfuric acid, except in areas immediately surrounding H_2SO_4 manufacturing plants is not present in sufficient quantities to cause agricultural damage. Near source emissions however, damage to foliage is a routinely observed phenomenon.

Sulfate in fact is generally regarded to be a necessary nutrient for many types of vegetation and to the best of this author's knowledge there is only one reported incident in which excessive sulfates and SO_2 intrusion to the ambient air resulted in a high enough sulfate content in the soil to cause extensive damage to epiphytic flora.[273]

Material damage due to air pollution causes serious economic losses and this fact is well recognized. Much of the damage to

structural materials, both non-metals and metals, correlates well with atmospheric acidity, unless maritime aerosols, which are also highly damaging, are present. The direct contribution of sulfuric acid or acid sulfates to this damage may not be as great as that of the substantially larger amount of SO_2 that is usually present but it must be remembered that the corrosivity of sulfur dioxide results from the ultimate formation and reaction of sulfuric acid. The works of Upham[506] and Tice[489] in this field have been the most notable, and generally excellent and specific references are available in a National Air Pollution Control Administration publication[502] as well as in an excellent article by Yocom and McAldin.[538]

Before the specific toxicologic appraisal of airborne sulfate is made, it is informative to discuss the phenomena of acid precipitation because acid precipitation is intimately associated with airborne sulfate and sulfur dioxide. Presently there is growing concern over the increasing acidity of rainfall and snowfall, and the problem has reached acute stages in Sweden and Norway. Tremendous decreases in fish population have occurred in both of these countries in recent years, and the decreases have been directly correlated with the increasing acidity of water in lakes and rivers. The matter was brought to the attention of the world when Swedish authorities officially lodged a complaint with the U.N. in 1972; the complaint was accompanied by long term studies by Swedish scientists that showed that by far the major portion of the air contaminants thought to be responsible for acid precipitation in

Sweden originates outside of the country. This is not the first instance* where dispute arose because the atmosphere of one nation was being used as a garbage dump for the pollutants of another country. As a result, massive studies have been initiated in the United Kingdom, which have been accused by the Swedish scientists to be the prime source of their problems. British scientists have continued to maintain that no siginficant amounts of airborne contaminants that have British origin are transported to Sweden.[461] Since the dispute is far from being resolved, it is likely to become a topic for international attention in the near future. A special report on acid precipitation sponsored by Chemical and Engineering News has been published recently and is an excellent source of general information.[283]

Pure water in equilibrium with atmospheric CO_2 has a pH of about 5.6, consequently acid precipitation has technically been defined to be rainfall and snowfall that have pH values below 5.6. Most scientists believe that the presence of sea salts, terrestrial dust, etc. and the absence of man-made particulate matter should give baseline pH values for 'normal' rainfall substantially higher than 5.6. There are, however, no historical data (from times when little or no man-made contaminants were present in the atmosphere) that corroborate this. The best available data indicate that prior to the 1930's, rainfall over the states of Tennessee, Virginia and New York was not acidic.[283] Currently the pH of

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*See for example the U.S. - Canadian dispute; Dean, R. S. and Swain, R.E., U. S. Bureau of Mines Bull., 453, 1944.

precipitation over much of the northeastern U.S. has mean annual averages around 4.0-4.2, and occasionally values as low as 2.1 have been observed.[282]

In a recent survey of the lakes of the Adirondacks in upstate N.Y., it was reported that over half the lakes had pH below 5 and in 90% of these fish no longer exist.[128] The effects in Norway and especially Sweden are far more devastating and widespread. Trout and salmon have become extinct in some 15,000 Swedish lakes, and an estimated 20% of all Norwegian territory has been affected.[225] Apparently newly hatched fish are very vulnerable to acid, and the death of eggs and young fish are thought to be the prime reason for the decline of the fish population. The situation is aggravated by the acid pulses brought about by the melting and thawing of snow because the first portion of the melt water is much more acidic than the bulk.[128]

What constitutes the acidity of acid precipitation? Using column and gas chromatographic techniques Galloway, et al.[168] attempted to assess the contribution of various organic acids and came to the conclusion that no more than 10% of the acidity is ever due to organic acids. After a decade long study at the Hubbard Brook experimental forests in New Hampshire, Likens and his coworkers concluded that sulfuric and nitric acids are almost entirely responsible for the observed acidity; the individual contributions of the two are about 60 and 40% respectively.[283] This conclusion is substantiated by the fact that in similar studies

done in Norway it has been observed that where the concentration of sulfate ions in precipitation was the highest, the pH of the rain and snow were the lowest, and the acidity of lake water was correspondingly high.[67]

There is little doubt about the origin of the sulfuric acid in acid precipitation. While part of it comes from the acid aerosol and the acid sulfates the rest must be produced from the oxidation of SO_2 dissolved in the rainwater by trace contaminants. The origin ultimately is easily traceable to the burning of fossil fuels, that is, the source of acid rain is almost totally anthropogenic.

Apart from the decline of fish population and obvious corrosion damages to structural materials, acid precipitation affects the aquatic ecosystem at all levels. According to Swedish workers,[225] the total number of life forms undergoes a drastic decrease with increasing acidity of the water in which they thrive; the most primitive life forms such as bacteria are affected the most seriously. As a result, the rate of decomposition of organic matter decreases and nutrient cycling from sediments is inhibited, and higher life forms decrease in population.

Likens[283] has further pointed out that if the pattern of increasing acidity continues in the terrestrial ecosystem, sooner or later sensitive vegetation is bound to be affected by acid precipitation; one single incident of acid rain during a specially sensitive growth stage (germination, flowering or fertilization) may very seriously affect the resulting crop. Unlike aquatic systems,

the land vegetation system is exposed directly to acid rain, and is not pretected by dilution with water. However, no soil has far greater reserves for neutralization of acids than do water masses and secondary effects are neither likely nor expected.

Toxicologic Appraisal of the Effects of Airborne Sulfuric Acid on Human and Animal Health

Studies of ambient air pollution are concerned mostly with the effects of air contaminants on human and animal health. Most of the studies on sulfuric acid, sulfates and sulfur dioxide have been done by two illustrious ladies, M. O. Amdur here in the U.S. and K. A. Bushtueva in the U.S.S.R. The approaches employed in the American and Russian laboratories for the toxicologic appraisal of these sulfur species, however, differ fundamentally.

While studies in this country have dealt with the incidence of acute and/or chronic respiratory disorders and with the pathologic changes due to longterm exposure, Bushtueva and other Russian scientists have been concerned almost entirely with the effect of these compounds upon sensory modalities, cerebral cortical functions and their interrelationships.

Fortunately, most of the pertinent Russian literature is available in English translation from the U.S. Department of Commerce.[280,428] Possibly the most informative source on this subject is a U.S. Environmental Protection Agency publication,[503] although it is somewhat outdated at the moment. Credit should also be given to Alarie and his coworkers from the Hazleton Laboratories in Vienna for the very thorough, long-term toxicologic

appraisals of sulfuric acid mist, SO_2 and particulate matter either alone or in conjunction with each other.[4,5]

It was originally believed[191] that the inhalation of sulfuric acid mist causes deleterious effects to the upper respiratory tract and that breathing such mist in gross quantities leads to death from edema or spasm of the larynx and inflammation of the upper respiratory tract. In contrast, sulfur dioxide was believed[154] to cause damage localized primarily in the lower respiratory tract. After the substantial amount of work done in recent years, it is understood that location of histopathologic changes associated with inhalation of the acid mist is dependent on the particle size of the acid aerosol. While it is largely true that effects of sulfur dioxide that is not associated with particulates are confined to the irritation of the lower respiratory tract, sulfur dioxide is almost always associated with particulates in the ambient atmosphere. The actual site of SO_2 attack varies with the nature and size of such particulate matter.

Since the physiological effects of air contaminants take place as a result of the inhalation of contaminated air, it is important to understand some basic facts about respiration. The amount of air breathed per minute at any given time is greatly dependent upon the amount of physical work being done at that moment. On the average, the amount of air breathed varies between six to a hundred liters per minute[202] and depends on whether the person is resting or doing some strenuous physical work. Intense physical activity is more likely to take place outdoors where air pollution and the

resulting hazards are greater than that indoors. The inhaled air travels through the nasopharyngeal region, then through the pharynx and larynx to the trachea and finally to the bronchi. The bronchi in turn consist of the bronchiole capillaries leading to the alveoli. The bronchi are parts of the lung proper and constitute the lower respiratory tract. When air containing particulate matter is breathed, the region where this particulate matter is preferentially deposited depends, not unexpectedly, on the size and mass of such particulate material. Particulate matter with MMD much greater than 10μ is filtered by the nose itself, and particles around or above 10μ seldom reach beyond the larynx. A substantial number of particles belonging to the large particle class travel to the alveoli through the tracheobronchial region where anything larger is trapped.[329] Particles that belong to the Aitken class also reach the alveoli. The alveoli presents a huge surface for deposition; on the average, the total alveolar surface is estimated to be around three quarters of a million square centimeters. The mechanism of alveolar deposition is not completely understood, but there is a deposition peak for particles that have a size around 1μ, and a minimum for those that have a size around 0.3μ and another maximum for particles of the Aitken range. Amdur in her classic paper,[17] categorically states that the toxicologic importance of submicron size particles cannot be overemphasized. The bulk of both the sulfuric acid and suspended sulfate burden of the ambient air definitely exist as submicron size particles. A semi-mathematical model has been developed from observed data

by Natusch, et al.[352] to show why the lung proper is the preferential deposition site for submicron size particles. A more mathematically rigorous model for half-micron size particle deposition during inhalation has been developed by Yang, et al.,[537] and has been substantiated by experimental data. The importance of the size of the inhaled aerosol particles can hardly be overexaggerated.

Amdur, who is beyond a doubt a leading authority on the general toxicology of sulfur oxides, has concluded that SO_2 by itself can be classified to be a mild respiratory irritant at worst.[11] This is true even at the threshold limit concentration (5 ppm or 13 mg/m^3). Sulfur dioxide, however, is a much more serious irritant when particulate matter, especially metal salt particulates, is simultaneously present in a humid atmosphere. Amdur investigated the possible potentiating ability of inert aerosols such as sodium chloride to aggravate the effects of SO_2 and concluded that some degree of potentiation is observed.[14] Later work, however, led her to conclude[16] that on an effect/unit concentration basis such potentiation is almost negligible in comparison with the effects of aerosols of manganese (II), iron(II) or vanadate ions, all of which, if the air is humid enough to permit their presence liquid aerosols, are capable of oxidizing SO_2 to H_2SO_4. After a study of potassium chloride and ammonium thiocyanate aerosols, which may be regarded to be inert like NaCl, and the available data on the solubility of SO_2 in saturated solutions of these salts, Amdur concluded that the potentiating effect of such

inert aerosols is primarily a concentration effect, i.e.; it is due to the increased concentration of atmospheric SO_2 in the solution phase. The humidity, needless to say, must be large enough to maintain these salts in the liquid aerosol state.

At the subacute level, Amdur's method of hazard evaluation has been the measurement of changes in pulmonary flow resistance (PFR) or in other words the change in the extent of work the lungs have to do to respire. It should be pointed out that an increase of 10% in PFR is almost insignificant and is usually imperceptible by the subject. With 5.5 mg/m^3 SO_2, and 10 mg/m^3 of NaCl aerosol, Amdur noted that the percent change in PFR (from control) is increased by a factor of about 2.4 in case of the aerosol + gas as compared to the gas alone. The gas alone at this concentration increases the PFR 20% from normal. With KCl and NH_4SCN at the same concentrations this factor was observed to be 3.3 and 5.0 respectively. The ratio of the effectiveness of these three aerosols at these levels can then be simply calculated to be NaCl: KCl: NH_4SCN = 1 : 1.4 : 2.1. The ratio of the equilibrium solubility of SO_2 in 3N solutions of these salts is 1 : 1.35 : 1.97.

Undoubtedly solubility is a key factor in such potentiation. This was further substantiated by Amdur in the same report; she showed that suspended particulates which are unable to form liquid aerosols such as oxides of iron or manganese, open hearth dust, etc., do not potentiate the effects of SO_2 as far as measurable changes in respiration characteristics go. Interestingly enough, carbon, whether activated or unactivated, exhibits no potentiating

ability. One would conclude therefore that potentiation of the effects of SO_2 by 'adsorptive concentration' is largely unsubstantiated.

On the other hand, using the catalytic aerosols Amdur found that even at concentrations one tenth of that used for NaCl aerosols the extent of observed potentiation was substantially larger than that observed with NaCl aerosols. These data all refer to studies with guinea pigs. In a recent study on the effects of SO_2, H_2SO_4 and industrial fly ash taken one at a time or in any given combination upon both guinea pigs and cynomolgus monkeys, Alarie, et al.,[5] have concluded that the deleterious effects, either long term or short term can be attributable to the acid alone. This conclusion is even more significant in view of the fact that this study was done with year or year and a half long exposures using probable ambient concentrations in polluted atmospheres, and not with unrealistically high concentrations. Therefore, no extrapolation of Alarie's conclusions is necessary. At this stage, referring to the so-called acute SO_2 pollution episodes, the question becomes very vital: which was the real culprit, the gas or the acid that formed from the gas?

Such a question, as will be pointed out in a later chapter, is more esthetic than anything else. After all, with the exception of direct sulfuric acid emission from sulfuric acid manufacturing plants and catalytic converter equipped automobiles, SO_2 must be present for H_2SO_4 to be formed.

The potentiation of SO_2 hazards by catalytic aerosols led Amdur

to investigate the effects of sulfuric acid mist directly. In her preliminary work,[9] she used aerosol sulfuric acid at various concentrations with MMD around 1μ. Eight hour LC_{50} (lethal concentration leading to death of 50% of test animals) varied between 18-50 mg/m^3 and it was dependent on the age of the guinea pigs used, the younger animals (about 18 months old) were far more susceptible. Although such concentrations are not likely to occur in ambient air, these experiments clearly established: a) sulfuric acid is orders of magnitude deadlier as an acute toxin than SO_2 (comparing in terms of equivalent concentrations), b) inhalation of sulfuric acid mist has two distinct effects, laryngeal blockage causing subsequent spasms and deep seated damage of the lung proper. The lung damage is cumulative and therefore some effects are expected to be observed on long term breathing of quite low concentrations of the acid aerosol. In a later study Amdur[12] experimented with sulfuric acid aerosols using concentrations between 2 - 40 mg/m^3 and particles that had MMD's of 0.8μ, 2.3μ and 7μ, respectively. The smallest particles were found to be far more effective than the others in causing respiratory stress. Even at the lowest concentration studied the 0.8μ MMD aerosol increased PFR by 50%; this is a much larger change than that observed for an equivalent concentration of SO_2. Decrease in dynamic compliance of the lungs was noted at the same time, and the respiration rate was observed to increase. Since particulate retention is inversely related to flow velocity and therefore breathing rate, Amdur suggests[17] that the increase in respiration rate may be a

reflex action of the lungs to protect itself. The larger particles did not display any significant effect at all except at the highest limit of the concentration range. This observation is readily understandable in view of the fact that the larger particles could not enter the tracheobronchial region. The concentration vs. response curves of sulfuric acid aerosol for various particle sizes are not linear and intersect. For this reason, it is impractical to make generalized statements regarding effects of particle size. However, for concentration levels likely to be encountered in ambient air, it may be stated that the effect increases with decreasing particle size.[17]

At this point it is also worthwhile to repeat Junge and Scheich's observation[249] that most of the free acidity in ambient urban air is associated with particles that have diameters lower than 0.1μ.

The effects of long term exposures (21 hours daily for 620 days) of 0.9 mg/m^3 H_2SO_4 ($\sim$ 0.5μ MMD) and 13.4 mg/m^3 SO_2 taken one at a time and in combination upon beagles has been reported by Lewis et al.[281] Artificial impairment was caused in some of the experimental animals by prior exposure to gross levels of NO_2. Surprisingly enough, the 'impaired' dogs fared better than the normal ones in every case, which led the investigators to conclude that a lung previously remodeled by a toxicant is more difficult to alter physiologically than one which has never been exposed to toxic concentration of air pollutants. This conclusion cannot presently be extended to humans with existing respiratory ailments

with any degree of certainty.

The most notable result of this rather extensive study that involved 32 dogs is a clear correlation between respiratory impairment and the presence of sulfuric acid aerosol. The acid aerosol significantly decreased carbon monoxide diffusion capacity, net lung volume, and caused substantial increase in total expiratory resistance. Total expiratory resistance is directly related to PFR. The chronic inhalation of the acid aerosol affected the conducting airways as well as the lung parenchyma. A decrease in lung and heart weights were noted upon postmortem examination.. Apparently neither the total body weight nor the weights of the spleen and the liver were affected. No gross pathological change of the lungs, however, was observed. The authors conclude that relatively low levels of aerosol sulfuric acid can produce serious pulmonary impairments and is far more effective in doing so than sulfur dioxide present in a far larger concentration.

These conclusions are well substantiated by the work of Alarie et al.[4] These workers studied a total of forty-five monkeys for eighteen months with H_2SO_4 concentrations of 0.4, 0.5, 2.4 and 4.8 mg/m^3 and the acid mist particles had MMD's 2.2, 0.5, 3.6 and 0.7μ respectively. Except for one particular exposure group (0.5 mg/m^3, 0.5μ MMD) pathological changes of the lungs, namely thickening of the walls of the bronchioles as well as the alveoli, and bronchiolar epithelial hyperplasia were observed in every case. The change was slight at the lowest concentration and severe at the highest. The investigators report that a concentration of

0.4 mg/m^3 with a MMD of 2.2μ is more hazardous than a concentration of 0.5 mg/m^3 with a MMD of 0.5μ. This is difficult to understand because results of other studies show increasing effects with decreasing particle size. It would appear therefore further investigations are necessary before any definite conclusions can be made regarding hazard index, concentration and particle size. Alarie, et al. have compared the results of this study with those obtained in their previous studies with NO_2, phosgene and sulfur dioxide and concluded that sulfuric acid is a deep pulmonary irritant like NO_2 and phosgene. At least 550 mg/m^3 of SO_2 would be necessary to produce a pulmonary response equivalent to the 0.4 mg/m^3 H_2SO_4 studied. In the same investigation the authors exposed a total of three hundred guinea pigs for a year to 0.1 mg/m^3 (2.8μ MMD) and 0.08 mg/m^3 (0.8μ MMD) H_2SO_4; no significant pathologic changes were noted upon post-mortem examination. The authors suggest that this is comparable to their previous studies on SO_2 exposure around the prescribed threshold limit of 13 mg/m^3.

Alarie, et al. conducted a more recent study[5] that has already been referred to. They exposed a hundred and seventy monkeys and four hundred guinea pigs to relatively low levels of SO_2 (0.8 - 40 mg/m^3), H_2SO_4 (0.1 - 1 mg/m^3 MMD 0.5 - 3.4μ) and fly ash ($\sim$ 0.5 mg/m^3, MMD $\sim$ 5μ) in various combinations for periods of a year and a half and a year respectively. No synergism was observed and the effects were attributable to the acid mist alone. No hematological or biochemical changes were observed and apparently growth rate also remained unaffected. Definite histopathological

changes in the lungs however, was revealed in every case of H_2SO_4 aerosol exposure, regardless of particle size. The effect was small around 0.1 mg/m^3 and pronounced at higher levels. Several other animal studies have been reported, primarily due to Bushtueva,[78-9] Thomas et al.,[485] Treon et al.,[495] and Pattle et al.[377] All these workers reached the same general conclusions on the basis of less extensive studies and would not be discussed any further.

For obvious reasons, the amount of data available in European and American literature on the controlled sulfuric acid exposure of human subjects is scant.

Apparently 'volunteers' are more plentiful in Russia. The bulk of these data however, are almost two decades old. In his treatise on industrial toxicology, Hamilton[193] rejected the idea that the incidence of brochial diseases in humans may be related to inhalation of sulfuric acid aerosol. Later work by Amdur et al.[10] clearly established that breathing of H_2SO_4 aerosol mist produces respiratory stress in human subjects. Approximately 1μ MMD H_2SO_4 aerosol was used, and the concentration was varied from 0.35 - 5 mg/m^3. Exposure time was varied from 5 to 15 minutes. On the average, 77% of the aerosol was retained in the respiratory system. This extent of retention is considerably higher than that observed for inert aerosol particles with the same size. Apparently the high hygroscopicity of sulfuric acid with the moist environment of the lung leads to greater retention. A likely hypothesis to explain the increased retention of highly hygroscopic aerosols

is that the relatively small size aerosol particles gradually grow in size as they travel down the humid respiratory tract and they are not exhaled easily thereafter.

Amdur, et al.[10] reported that even at the lowest concentration studied (0.35 mg/m^3) respiratory stress was indicated by shallower breathing (lower tidal volume) and increased respiration rate. The speed of onset and the extent of the effect was dependent on the concentration. While any concentration lower than the recommended TLV of 1 mg/m^3 was not perceptible by the subjects themselves, all subjects detected the presence of contamination when the concentration was increased to 3 mg/m^3. Fifteen healthy males were chosen as subjects and to prevent any psychologic effects the apparatus was hidden from their view. Further, the exposures were started and stopped at times unknown to the subjects.

Morando[3,4,5] came to the same conclusions using the same concentration levels and exposure times. He reported however, a lower threshold of detection (0.5 - 0.7 mg/m^3). Sim and Pattle's study[4,5,7] came next but the concentration levels used by them were so high that any extrapolation to ambient levels may be tenuous. These workers used an acid mist that had particle sizes between 1μ and 2μ and reported that for a given concentration, larger particles with lower acidity cause greater respiratory stress than smaller particles with higher acidity. These workers also reported their increased sensitivity towards the acid mist as a result of the study they had conducted. At the end of the study period of 10 months, one of them developed a moderately severe but

extremely persistent bronchitis. The increased sensitivity of his physiologic system resulted in intense bouts of coughing and wheezing when he was exposed to the acid mist, however slightly. Bushtueva[77] studied ten subjects using sulfuric acid aerosol of unspecified particle size and concentrations up to 6 mg/m^3. The limit of perception as evidenced by the onset of laryngeal irritation started around 1.1 mg/m^3. Between 1.1 and 2.4 mg/m^3, all subjects experienced irritation at the base of the esophagus and several complained about irritation of eyes. Above 2.4 mg/m^3, all subjects experienced severe irritation of the mucous membranes and eye mucosa. These levels also triggered intense coughing, presumably due to a reflex mechanism. She also reported distinct reflex changes in respiratory rhythms and related processes at all concentrations over 1 mg/m^3, the extent of the effect increased with increasing concentration. The study of Toyama and Nakamura[493] appears to be the last reported work on controlled exposure of human subjects. Their study involved particles ranging from 1.8μ to 4.6μ in MMD and they reported that substantially larger changes in PFR values are caused by the smaller particles. These workers reported onset of increases of PFR values at levels as low as 0.01 mg/m^3, but these data seem to be doubtful.

To summarize the studies of respiratory stress caused by inhalation of aerosol sulfuric acid, the fact must be pointed out that these studies were done with young healthy adults, whose ability to compensate for the stress is much higher than very young children or aged people or persons already burdened by

cardio-respiratory deficiencies. Increased PFR values for the very young and the aged are likely to bring about bronchospasm even at low levels, leading to the same general symptoms of wheezing, increased secretions, dyspnea, spasmodic coughing, chest pains, increased respiratory rates (both due to reflex action and impaired gaseous exchange in the alveoli) that are observed in the healthy subjects at higher levels.

Russian scientists have studied in great detail the effects of aerosol sulfuric acid, either by itself or in conjunction with SO_2, upon the interrelationship of sensory modalities and cerebral cortical functions such as optical chronaxy (time threshold necessary for the appearance of light sensation), dark adaptation (intensity of light necessary for detection after adaptation in complete darkness), alteration of alpha-rhythm (monitored by continuous electroencephalography) and general conditioned reflex. An account of this work is given in the EPA publication[503] edited by Amdur and others. The toxicologic significance of such studies is uncertain at best. In terms of limits of detection, the perception threshold varies between 0.6 - 0.8 mg/m^3 H_2SO_4 for either suppression of dark adaptation, elevation of optical chronaxy or disruption of alpha rhythms. This concentration also happens to be roughly the odor threshold for the acid aerosol as well as the threshold for the onset of mucosal irritation. Somewhat lower levels (0.4 mg/m^3) are perceptible through changes in the electrocortial reflex.

Effects of Particulate Sulfate

The fact that sulfates constitute a large part of the atmospheric aerosol burden is relatively recent knowledge and the amount of data available on their toxic effects is scanty. The species that have been studies are mangananese (II) sulfate, zinc sulfate, ammonium sulfate, zinc ammonium sulfate, iron (II) sulfate and iron (III) sulfate. Using concentrations of 1 mg/m^3 neither manganese (II) sulfate nor iron (II) sulfate was found to cause any perceptible change in respiratory parameters. In contrast, the same concentration of iron (III) sulfate was found to cause a 77% increase in PFR in guinea pigs exposed for an hour. Using roughly the same concentration both ammonium sulfate and zinc sulfate aerosols were found to increase pulmonary flow resistance several times more than that caused by an equivalent amount of SO_2. Between zinc sulfate and ammonium sulfate, the former was found to be the more hazardous.[18]

Zinc ammonium sulfate appears to be the most thoroughly studied sulfate salt in this context. The interest in this compound probably originated after its presence in substantial quantities was reported during the acute pollution episode in Donora, Pa. According to the studies of Amdur and Corn,[15] as a respiratory irritant this compound has the same order of potency as aerosol sulfuric acid, a factor of two greater than zinc sulfate and about 3 or 4 times greater than ammonium sulfate. The extent of pulmonary effects increases linearly with decreasing particle size (range studied 0.3 - 1.4μm MMD) and increasing concentration (up to

4 mg/m^3). Using a concentration of 1 mg/m^3 the 0.3μ MMD aerosol was found to increase PFR by 80%; this increase is an order of magnitude greater than that produced by an equivalent concentration of SO_2. Nadel[349] studied the effects of zinc ammonium sulfate on cats. Very short exposure times (3 mins.) and high concentrations (40 - 50 mg/m^3) of the aerosol was used in this study. The same general symptoms reported by Amdur and Corn for guinea pigs exposed longer to lower concentrations were observed.

Apparently no studies have been done on ammonium bisulfate. Intuitively one would guess that as a respiratory irritant this compound probably poses the same degree of hazard as sulfuric acid aerosol. Exhaustive data are also sorely needed to substantiate the effects of ammonium sulfate aerosol of various size classes and different concentrations, especially because ammonium sulfate is quite often the prevalent compound in ambient air.

SOME ACUTE EPISODES

Meuse Valley, Belgium, 1930: Week long adverse weather conditions precipitated a severe pollution episode in this highly industrialized area containing coke ovens, blast furnaces, steel mills, glass factories, smelters and sulfuric acid plants. Respiratory illness was widespread and led to 60 deaths that were attributed to the polluted air.[317] Firket[155] commented prophetically that if such an episode were to occur at London, there could be 3200 excess deaths. Suspected culprits: Sulfur dioxide and related oxidation products.

Donora, Pennsylvania, 1948: Five day long adverse weather conditions precipitated an episode in this relatively small town that

was to be etched in every resident's memory forever. Twenty people died of respiratory afflictions. Many, many more were ill. The surrounding industries included a steel mill, a large zinc production plant and a sulfuric acid plant.

Suspected culprits: Sulfur dioxide and related oxidation products, zinc salts and fluorides(?).[498]

London, England, 1952: Firket's prophecy was just a little short of what was to happen. Not 3200 but approximately 4000 excess deaths attributable to deteriorated air quality occurred during a five-day episode of severe fog and pollution. Extremely adverse weather conditions and moderately severe pollution episodes leading to measurably excess deaths were not new to Londoners. Such episodes have been recorded for the years 1873, 1880, 1882, 1891, 1892 and 1948. However, not a single one had ever reached the catastrophic proportions of the '52 episode, and since then, although relatively minor episodes have occurred in 1959 and 1962, the Londoners have been spared the magnitude and horror of the massive pollution that stopped the city in 1952.*

Suspected culprits: Sulfur dioxide, sulfuric acid, suspended sulfates.[496]

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*Interestingly enough some 700 years ago the Queen of England moved her residence from London to Nottingham to get out of the polluted air. Another 300 years later the kind Westminister brewers offered to burn wood instead of coal because of Queen Elizabeth's allergy to coal smoke. At one time legislation was passed prohibiting the use of coal in the city of London while the parliament was in session.[50] Referring to the recent English-Swedish disputes in the U.N., it would appear that the English still have a long way to go.

New York City, 1953: Statistically significant number of excess due to respiratory and related afflictions were reported during and after a five-day pollution episode.

Suspected culprits: Sulfur dioxide and uncharacterized particulate material.[500]

Eastern United States, 1962: Outbreak of respiratory disorders and a number of excess deaths attributable to poor air quality were recorded in Washington, Philadelphia, Cincinnati and New York City.

Suspected culprits: Sulfur dioxide and uncharacterized particulate material.[501]

London, England, 1962: Seven hundred excess deaths occurred. Concentration of particulate material was less than the 1952 episode.

Suspected culprits: Sulfur dioxide, sulfuric acid and suspended sulfates.[446]

Rotterdam, Netherlands, 1962: A severe outbreak of respiratory disorders was observed. The measured SO_2 level rose to five times its normal value. Some excess deaths and large scale absenteeism was also reported.

Suspected culprits: Sulfur dioxide and related oxidation products.[246]

Hamburg, Germany, 1962: The situation was identical to Rotterdam. In addition to increased levels of SO_2, measured values indicated a doubling of concentration of particulate matter. Hospital admission for respiratory diseases and death due to such causes became high.

Suspected culprits: Sulfur dioxide and related oxidation products.[180]

Osaka, Japan, 1962: Sixty excess deaths occurred due to a four-day

air pollution episode.

Suspected culprits: Sulfur dioxide and uncharacterized particulate matter.[180]

Community Health Studies

Epidemiologic studies, unlike experimental toxicology, deal with the actual environment and therefore are inherently superior for evaluation of hazards. The problem with such studies, however, is that neither the factors are controllable, nor is there a high probability of relating a single event to a single cause. Epidemiologic studies by their own virtue are based entirely on statistical correlation.

Details of different epidemiologic studies conducted in various parts of the world have been published.[502] There is no doubt that death and illness due to respiratory disorders is well correlated with high levels of sulfur dioxide and particulate matter. In most of these studies available techniques did not permit reliable measurement of sulfuric acid and other sulfate aerosol levels. From our previous discussions, however, it is obvious that these compounds are bound to be associated with sulfur dioxide and particulate matter, especially under adverse weather conditions.

In recent years simple techniques became available for measuring suspended sulfates. In urban areas a strong correlation was observed between industrial absenteeism due to respiratory illness and the atmospheric sulfate level.[129-30] A similar correlation apparently exists for school absenteeism as well.[20]

Starting in 1968, EPA, in collaboration with public health authorities, began its CHESS (Community Health and Environmental Surveillance System) program. From the reports already available[455] there seems to be little doubt that a correlation exists between the concentration of suspended sulfate and the frequency of incidence of acute and chronic respiratory disorders in adults as well as children. This report also states that in urban areas sulfate aerosol pollution risk factors may be as high as that involved in cigarette smoking.

Because of a number of difficulties (to be described in Chapter V), it is still not possible to measure sulfuric acid accurately in the ambient air. Sulfuric acid has been shown to be a more hazardous contaminant than most suspended sulfates and sulfur dioxide.

There is no question that an urgent need exists for better analytical methods in conjunction with size discriminating samplers for the specific determination of airborne sulfuric acid and sulfates so that the effects of actual urban levels of aerosol sulfuric acid and sulfate may be studied on a epidemiologic basis.

CHAPTER IV

THE DETERMINATION OF AQUEOUS SULFATE

"A man would do nothing if he waited until he could do it so well that no one would find fault with what he has done."

- Cardinal Newman

A fast and sensitive aqueous sulfate determination technique was first developed during the course of the present work. Because most routine airborne sulfate determinations involve the determination of the total soluble sulfates collected on the sampling filter after dissolution, a review of the methods for determining aqueous sulfate is presented.

Quite aside from the environmental aspects of determining aerosol sulfuric acid and other sulfates in air, determination of sulfate in water, especially in trace quantities has offered a challenge to researchers for a long time. In terms of time, effort and ingenuity, it is doubtful whether any other anion has received so much attention. The available literature contains literally hundreds of reports that describe 'new' methods of determining sulfate and several hundred more that propose minor modifications to existing ones and/or describe their applications in real situations. It is almost impossible to write an exhaustive review of the available literature on the determination of aqueous sulfate and in this chapter only the highlights will be considered.

A remarkably thorough review of aqueous sulfate determination procedures has been given by Thoma[483] in a recent dissertation, and the more interested reader is referred to this source.

High sulfate concentrations in drinking water leads to gastroenteritis in children[101] and in general high levels (> 600 ppm) exert Cathartic effects.[337] Excessively high levels (~ 1000 ppm) leads to hypocalcaemia, hyperphosphataemia (suggesting parathyroid hypofunction), low urinary pH (leading to uric

nephrolithiasis) and massive urinary sulfate excretion and metabolic acidosis.[58] U.S. Public Health drinking water standards[479] state a maximum allowable concentration of 250 ppm in drinking water. However, the interest in determination of aqueous sulfate, especially in trace quantities, can hardly be attributable to the study of animal and human health effects because the regulatory standards have been introduced only relatively recently and further, the determination of sulfate concentration greater than 100 ppm is not generally regarded as a problem.

One may justifiably conclude that the real reason behind the early interest in developing trace aqueous sulfate determination procedures was more esthetic than anything else.

Following the discovery of native barium carbonate (witherite) in 1782, Withering[535] proposed the barium sulfate precipitation test for sulfate in 1784. Even to this date the simple gravimetric determination as barium sulfate remains the reference method for the determination of sulfate. Perhaps this fact alone is enough of a challenge to the innovativeness of mankind and new sulfate determination methods are continuously being developed.

In the following description, the various sulfate determination methods (including the more important modifications) has been broadly classified on the basis of the chemistry involved rather than on a basis of specific instrumentation. Hopefully, this would give the reader a better perspective and would show how little new chemistry was involved in the developmental process encompassing almost two hundred years. At the end of this chapter

a flowchart depicts the essence of the various aqueous sulfate determination methods.

A. Methods Involving Precipitation of an Insoluble Sulfate or The Formation of a Sulfato Complex

A-I. Methods Dependent on Formation of Insoluble Barium Sulfate

Roughly 80% or more of all methods developed fall into this category. This is not surprising in view of the fact that barium sulfate is the most insoluble sulfate (solubility 2.46 mg/l at 25°C)[522] known.

A-I.a. Gravimetric Method

This is the time tested sulfate determination procedure without a description of which even the most humble text on analytical chemistry is incomplete. The gravimetric method has been designated as the preferred or the standard reference method by ASTM[33] and also the most accurate method by APHA, AWWA and WPCF[479] for sulfate concentrations of 10 ppm and above. A description of the procedure is available in any standard text or analytical manual. The main errors involved arise primarily from coprecipitation of undesired anions/cations, barium sulfate being one of the best known carriers. A detailed account of the errors involved in the gravimetric sulfate determination is given in Kolthoff and Sandell's classic text on analytical chemistry.[260]

A-I-b. Turbidimetric and Nephelometric Methods

The first turbidimetric method was reported by Hinds[206] at the turn of the century. He used a candle as the light source, a graduated cylinder as a variable pathlength cell and the eye as the

detecting device. Jackson[229] made several modifications to Hind's crude instrument and improved the reliability of the method. The only other noteworthy turbidimetric method that used the eye as a detector is that due to Sheen, et al.[452] who designed an ingenious apparatus. They illuminated the barium sulfate suspension by a light bulb. The transmitted light went through a slit system to an eyepiece and the scattered light was reflected to a second eyepiece. The operator visually compared the two intensities and adjusted the slit until they were the same. Standard calibration curves were drawn in terms of the numerical setting of the slit.

Precision and reproducibility improved at this time as a result of the availability of a photometric detector and the need for conditioning agents to promote uniformly sized barium sulfate particle formation was recognized. During this period, Hibbard[204] appears to be the last to report a barium sulfate turbiditimetric method without use of an additive and Owe[375] the first worker who introduced them. Hydrochloric acid by itself or in conjunction with sodium chloride was generally used and numerous reports were published that claimed improvements with more exotic suspending agents. Some examples are: glycine-gum arabic,[515] gelatin,[243] glycerol-glucose-hydrochloric acid,[97] ethanol-dipropylene glycol,[491] magnesium chloride-sodium acetate-potassium nitrate-acetic acid,[424] etc. Currently the APHA standard method[479] uses glycerol-ethanol-hydrochloric acid-sodium chloride as the conditioning reagent.

Reporting slight modifications that claim some improvement in an otherwise established procedure has been the rule rather than

the exception among the various reported sulfate determination methods. To what extent actual improvements were achieved and was not simply the bias of the experimenter is anyone's guess. The climax in this particular instance was reached with the relatively recent (1968) report of Wimberley.[564] He categorically stated that additives serve little purpose and recommended that additives be altogether dispensed with since fewer manipulations are required when no additives are used.

The first reported use of a spectrophotometer in barium sulfate turbidimetry seems to be that of Thomas and Cotton.[261] They carried out their measurements at 380 nm using 1 cm cells. Since then various wavelengths and path lengths have been used for measurement.[97,261,424,534] The APHA standard method[479] specifies a measurement wavelength of 420 nm and a 4-5 cm pathlength cell.

A-I-c. Titrimetric Methods

Initially, titrimetric methods for determining sulfate were developed because of a need of a faster and less tedious method than gravimetry. So many different titrimetric approaches have been developed that some subclassification is necessary.

A-I-c-1. Indirect Titrimetric Methods: Three broad classes of titrimetric approaches can be immediately recognized. Chronologically the first class comprised of the indirect methods in which the sample solution containing sulfate is treated with a second and somewhat more soluble barium salt (as compared to barium sulfate), such as chromate, iodate, oxalate phosphate, carbonate, stearate, palmitate and lauryl sulfate. Respective solubilities in mg/l are:

3.4, 80, 93, data not available, 20, 40, 40 and data not available.[522] Either a one-step or a two-step precipitation process was used. The one-step process involved direct treatment of the sample solution with the insoluble salt. The two-step process involved treatment of the sample solution with an aliquot of a barium salt (usually barium chloride), to precipitate barium sulfate which may or may not be filtered off at this stage. It was then followed by an aliquot of the anion (generally in the form of its alkali metal salt) in an amount equivalent to the amount of barium added. This anion forms an insoluble salt with barium. Barium sulfate, being less soluble than any other barium salt does not undergo methathesis and a corresponding amount of the added anion remains in solution. After the precipitate is filtered off, this anion or its hydrolysis product, (generally the hydroxyl ion) is then titrated using various types of analytical finish.

A-I-c-1a. Methods Using Barium Chromate: By far the largest number of indirect titrimetric methods utilize barium chromate. It is attractive because of its low solubility (almost as low as barium sulfate), the fact that it can easily be dissolved in acid without destroying the anion (cf. carbonate) or precipitating the corresponding acids (cf. stearate, palmitate). The intense color of the chromate anion and also the capability of the latter to function as a strong oxidizing agent made determinations via chromate attractive.

The first reported method using barium chromate seems to be that due to Andrews[21] who treated the sample solution with a

solution of barium chromate in acid, neutralized it, and filtered off the barium sulfate and the barium chromate. He then determined the chromate in the filtrate iodometrically using standard sodium thiosulfate and starch indicator.

Smith[462] modified this one step process into a two step precipitation process, first precipitating the sulfate with a known aliquot of standard barium chloride followed by an aliquot of standard potassium chromate (or dichromate[264]) in excess. As before the precipitated solids were filtered off and the chromate was determined by iodometry. A careful control of pH was necessary to ensure complete precipitation of barium chromate.

As alternatives to the iodometric determination of chromate, various other methods have been reported. They include: titration with a standard solution of iron (II) (using ferricyanide[419] or ferroin[169] as indicator), standard barium ion solution[232] (endpoint: disappearance of yellow chromate color from the solution. Other endpoint detection methods utilized in direct titrimetric methods are also applicable, see section A-I-c-3) and standard tin (II) solution (mercury (II) chloride indicator).[402]

Andrews[22] developed what is probably the most complex indirect titrimetric procedure that involved barium chromate. He treated the sample with a mixture of sodium acetate and barium chromate, adjusted the pH to basic; boiled and filtered off the precipitate. He then acidified the filtrate and reduced it to chromium (III) with an excess aliquot of standard iron (II) solution and back titrated the excess iron with standard permanganate.

The chromate methods were subject to a number of errors,[322] arising primarily due to the interference of other anions that form insoluble barium salts, especially phosphate. Other indirect methods were developed primarily in an effort to minimize or eliminate these errors.

A-I-c-1b: Methods Using Barium Carbonate: Howden[217] introduced barium carbonate to replace barium chromate in a one step precipitation process. The sample was boiled with barium carbonate, the solids were filtered off and the carbonate in the filtrate was determined by alkalimetry using a solution of standard hydrochloric acid and methyl orange[217] or phenolphthalein[361] as indicator.

Shinkai[454] modified this one step process to a two step process. He used an aliquot of standard barium chloride to precipitate the sulfate first, filtered it off and added an excess aliquot of standard sodium carbonate. The mixture was filtered again and the excess carbonate was then determined by alkalimetry with standard hydrochloric acid and methyl red indicator.

A-I-c-1c. Methods Using Other Barium Salts: Liberated oxalate ion from barium oxalate has been determined by standard permanganate[407] and liberated iodate ion from barium iodate by iodometry. In the barium iodate procedure the sample was treated either directly with barium iodate[464] or percolated through an ion-exchange column containing barium iodate.[267] In a two step process Davey, et al.[118] precipitated barium lauryl sulfate and titrated the excess lauryl sulfate with benzalkonium chloride using methyl yellow indicator. A rather involved procedure that

was developed in the late twenties,[504] employed barium phosphate. The liberated phosphate was determined by precipitating it as phosphomolybdate, dissolving the precipitate in an aliquot of standard sodium hydroxide and determining the excess base. Colorimetric methods of determining phosphate as molybdenum blue via phosphomolybdate have been introduced only relatively recently.

A-1-c-2. Semidirect Titrimetric Methods: These methods succeeded the indirect titrimetric methods and involved the addition of an excess aliquot of barium ion solution to the sample to precipitate the sulfate. The excess barium was then determined, after/without removing the precipitated barium sulfate, by titrating it with an anion that forms an insoluble barium salt.

Chromate again was the titrant of choice, the first reported method was that due to Jellinek[233] and it required careful pH adjustment. At the end point the additional chromate hydrolyzed enough to cause a change in the color of methyl red used as indicator. Color change, however, was indistinct and external indicators such as benzidine,[132] p,p'-diaminodiphenylamine,[425] lead nitrate,[174] etc. were preferred. As electrochemical methods were developed, the chromate titrimetric methods enjoyed a rebirth because it became possible to locate the end point potentiometrically[516] and amperometrically.[482]

Among other titrants used were carbonate,[442] stearate,[34] palmitate[42] together with suitable pH indicators. Interestingly enough, sulfate itself was used as a titrant in a number of methods using rhodizonate as the indicator,[120,343,348,473] the red

color of barium rhodizonate disappeared at the end point. The method involved a back-titration because rhodizonate cannot be used successfully as an internal indicator in the direct titration. More recently, variamine blue has been recommended[203] to be the best indicator for the back-titration with sulfate.

Determining the excess barium complexometrically was a popular approach. The original complexometric method[347] was rather involved because magnesium and calcium present in the sample had to be determined first. Belcher, et al.[55] suggested some variations but the first real improvement was due to Sijderius[457] who removed the interferring cations by an ion-exchanger. A host of complexometric procedures then developed. In addition to the commonly used disodium salt of ethylenediaminetetraacetic acid the tetrasodium salt was also used.[90] Another important titrant was the trisodium salt of diethylenetriaminepentaacetic acid (DTPA).[521]

Although Eriochrome Black T (Erio-T) was by far the most popular indicator, other indicators such as naptholphthalein,[90] calcein,[144] phthalein purple,[303] etc. were also used. One of the most interesting indicators that was used with the complexometric approach was the fluorescing indicator fluorexon:[86,362] titrations in this case were carried out under UV illumination.

A-I-c-3. Direct Titrimetric Methods: The first few years of direct titrimetry did not enjoy a great deal of popularity. Use of indicators was primarily limited to rhodizonate as an external indicator[175] and tetrahydroxyquinone.[443] In an unusual direct

titrimetric procedure with barium hydroxide as titrant, fluorescein in the presence of trace Mg^{+2} and Mn^{2+} was used an indicator.[324] Magnesium hydroxide and Manganese (II) hydroxide formed an adsorption complex with the dye only in the absence of sulfate. Methods employing tetrahydroxyquinone showed some promise and several modifications that involved changes in reaction medium, pH, addition of other dyes and metal ions were proposed. (Many workers, however, still preferred to use tetrahydroxyquinone as an external indicator.[25,194,275,370,453]) The search for better indicators continued and alizarin red S,[163] thorin,[164,335] and stilbnapthazo[326] came next, to be followed by a serios of bis(phenylazo) derivatives of chromotropic acid.[48,73-4,251-2,265,360,365,385,429,437] Of these later classes of indicators sulphonazo III[72] is the most popular today;[314] for a detailed discussion of reaction media, etc. the interested reader is referred to Thoma's dissertation.[483]

As electrochemical methods were developed, conductometric[427] and high frequency oscillometric[230,341] direct titrations became popular. Because of the much lower ionic mobility of the acetate ion, barium acetate was preferred to barium chloride as titrant. Potentiometric titrations using a barium sensitive $Mo/MoO_3//BaSO_4$ electrode was also developed.[339] Attempts to construct and utilize a sulfate sensitive membrane electrode were not very successful. The first reported electrode of such kind could only be used in a reverse titration.[395] (See semidirect titrations, sec. A-I-c-2). Very recently however, better electrodes have become commercially available.[100,449] Although they suffer from

a number of anionic interferences, they can be used in either direct or reverse titrimetric procedures.

Thermometric methods of detecting the end point are actually over half a century old,[121] but they have been popular only recently[136,531] now that instrumentation to detect small thermal changes are available.

A-I-d. General Indirect Methods: These methods do not involve titrations but still utilize the liberation of an anion from its insoluble barium salt via the formation of barium sulfate. The analytical procedure to determine the anion has generally been spectrophotometry, and to achieve accuracy, removal of cations through ion-exchange is necessary. A useful technique[38] in this context was the addition of pure solid barium sulfate. The barium sulfate acted as a carrier and thus ensured the completion of precipitation.

Barium chromate was again the first compound to be used, the chromate being determined directly[70,228] or after reaction with s-diphenyl carbazide for increased sensitivity.[228,507] Sometimes the method was elongated into a two step precipitation[145] process that involved the use of potassium dichromate as the second precipitant. Potassium dichromate is a better primary standard than potassium chromate. Measurements, however, had to be made after pH adjustment. Liberated chromate has also been determined polarographically.[333] Important among other salts of barium used were rhodizonate,[40] violurate,[268] chloranilate,[59] (also determined polarographically),[218] and the methyl thymol blue complex of

barium.[263] The chloranilate method is in common use today[440] and automated versions are available.[167] With the methyl thymol blue method, either the increase in absorbance of the free dye[270] or the decrease in absorbance of the metal-dye complex[310] can be monitored. In addition, the method can be modified easily for automated procedures.[2,310]

Barium iodate has also been used in non-titrimetric indirect procedures, the iodate being determined polarographically,[219] or radiometrically[65] (using I-131 labelled barium iodate).

A-I-e. Semidirect Methods: Semidirect non-titrimetric methods involved the addition of an aliquot of barium and the excess barium was then determined spectrophotometrically. Usually a suitable dye was added and the absorption due to the barium-dye complex was measured. Thorin has been used in a sensitive automated method[380] and virtually every dye of the bis(phenylazo) chromotropic acid family listed under indicators for direct titration has been used. (See Flowchart 1) Ref. 314 and references therein are recommended for details. Atomic absorption[141] and flame emission,[76,451] have also been used to determine the excess barium.

A-I-f. Miscellaneous Methods Involving Barium Sulfate: Precipitated barium sulfate has been dissolved in ethylenediaminetetraacetic acid (EDTA) and the sulfate determined either by measuring the excess EDTA titrimetrically[55] or by measuring the barium through atomic absorption[319] or flame emission.[113] A popular radiochemical approach was to add S-35 labelled barium sulfate

of known specific activity as carrier and then measure the specific activity after precipitation. Another radiochemical technique involved the use of an aliquot of Ba-133 labelled precipitant and a total count of the supernatant liquid[257] was made after settling of the precipitate.

A novel electrochemical approach involved the use of an iron selective electrode. In this method, a small excess of iron (III) was added to the sample upon which the sulfato complex of iron (III) was formed. The solution was then titrated with barium ion, while monitoring the concentration of the iron (III). Barium sulfate was formed and the iron (III) was decomplexed. The titration was taken to be complete when no further increase in free iron (III) concentration occurred.[231]

Absolute conductance measurements have been used; measurements were made after the sample was treated with an aliquot of standard barium chloride solution.[388] In another technique, prior to conductance measurement, all metallic cations were removed from the sample by ion exchange and then almost all anions other than sulfate were removed by treatment with solid mercury (II) oxide.[236]

For samples containing excessive amounts of chloride, Mascini[328] has described the use of a silver-form cation exchanger followed by a H^+-form exchanger. The first exchanger removes the chloride and the second exchanger removes any silver thus introduced. Direct estimation of sea-water sulfate content is impossible by most methods without prior removal of chloride.

Of all the properties used to determine sulfate, probably the most unique was measuring the volume of the barium sulfate precipitate.[28,492] The most sensitive quantitation technique (limit of detection 5 ng sulfate) on the other hand, was a ring oven method,[43] based on Feigl's original spot test.[151] The method involved the liberation of rhodizonate from Ba-rhodizonate by sulfate, washing the rhodizonate to ring zone and developing the color by reacting with barium ion.

A-II. Methods Involving Lead Sulfate: Lead Sulfate is more than an order of magnitude more soluble than barium sulfate (solubility 42.5 mg/l at 25°C).[522] Yet, many methods have been developed involving the formation of lead sulfate, because of the different chemistry of the lead ion. Naturally, there are no gravimetric methods because there are no advantages over barium sulfate precipitation in choosing such a route.

A-II-1. Tritrimetric Methods: Titrimetric methods based on the formation of lead sulfate comprises the largest portion of the methods that involve the lead ion. Unlike barium, no indirect titrimetric methods have been developed because, as stated earlier, there are no advantages.

A-II-1a. Semidirect Methods: Semidirect methods involve the addition of an aliquot of lead ion and then back titration of the excess lead after or without filtering the lead sulfate.

The excess lead has been titrated with potassium chromate using s-diphenylcarbazide as external indicator.[366] The light emitting indicator siloxene[255] was used as an internal indicator

for the same titration. The titration was also carried out potentiometrically using a standard glass electrode.[89] The excess chromate ion hydrolyzed at the end point and caused a change in pH. Another potentiometric procedure used sulfide or thioacetamide as titrant[510] and used a sulfide selective electrode.

Sulfate itself has been used as a titrant, together with dithizone as indicator.[353] Supposedly, the color change in the reverse titration is easier to perceive that with the direct mthod. Another interesting titrant used was molybdate, with tannin as the indicator.[152]

Complexometric titrations to determine the excess lead enjoyed some popularity. The usual EDTA titration employed xylenol orange[367] as indicator. Alternatively, the precipitated lead sulfate was dissolved in an excess aliquot of EDTA and the excess EDTA back titrated with standard zinc (II) using eriochrome black-T as the indicator.[122]

A-II-1b. Direct Titrations: The direct titration of sulfate with lead ion were developed much before direct titrimetric methods employing barium became available. Iodide ion[344] and eosin[404] were two of the first indicators employed. Diphenylcarbazone[355] and PAR[4-(2-Pyridylazo)resorcinol][389] were suggested later as internal indicators, but rather strict pH control was necessary. Possibly dithizone[356] was the best choice, especially when photometric detection of the end point was employed.[358]

Among instrumental approaches to direct titration most noteworthy were amperometry at the dropping mercury electrode,[259]

potentiometry employing lead selective electrodes,[405,423] and high frequency oscillometry.[230]

A-II-1c. Other Titrimetric Methods: These methods are primarily complexometric. An important example of such a method is one that involves the dissolution of precipitated lead sulfate in sodium acetate and titrating the lead with EDTA using xylenol orange as indicator.[367]

A-II-2. Non-titrimetric Semidirect Methods: In these methods the excess lead is determined after precipitation of lead sulfate. The analytical procedures commonly used are atomic absorption[286] and polarography.[371]

A-II-3. Other Non-titrimetric Methods: These methods involve the dissolution of precipitated lead sulfate and measurement of the lead concentration. Lead sulfate was dissolved in sodium hydroxide, sodium sulfide was added and the resulting lead sulfide suspension was quantitated by colorimetry.[276] Alternatively, lead sulfate was dissolved in ammonium acetate and the lead ion was determined by polarography.[330] Atomic absorption has also been employed, after dissolving the lead sulfate in EDTA.

A-III. Methods Involving Thorium and Zirconium Sulfates: These methods rarely involve actual precipitation; the salts themselves are too soluble to be precipitated, unless gross concentrations of sulfate are present. The stable sulfato complexes of the metals are actually formed and this property is utilized in the determination of sulfate.

A-III-1. Addition of Sulfate to Thorium or Zirconium Complexes With Dyes: In these methods the free dye is liberated from a thorium or zirconium dye complex by forming the sulfato complex. Either the absorbance due to the free dye or the decrease in absorbance due to the metal-dye complex is measured. The respective absorption maxima are usually well separated in wavelength. Among the more important dyes used were pyrocatechol violet,[376] alizarin red S,[376] eriochrome cyanine R,[376] acid chromium blue K,[39] alizarin,[39] SPADNS [3- (p-sulfophenyl)azochromotropic acid],[210,376] xylenol orange,[376] morin,[350] flavonol,[351] and amaranth,[266] of which the last one can be used with thorium only.

Both morin[189] and flavonol[351] have been used also in fluorometric procedures. The decrease in fluorescence of the metal-dye complex is measured.

A-III-2. Other Spectrometric Methods: Other methods that involve the sulfato complexes of thorium and zirconium has been developed; these differ slightly from the methods described so far.

Of the more important procedures, mention should be made of the thorium-salicyl fluorone[354] and the zirconium-calcein blue[475] methods, both are fluorometric. In the first, the sample is treated with an aliquot of thorium followed by an aliquot of the dye. The fluorescence due to the free dye is measured. The second method is based on the fact that sulfate actually enhances the fluorescence of the zirconium-calcein blue complex apparently through the formation of a complex that contains the sulfate, the dye and the metal ion.

A-III-3. The Zirconium-Methyl Thymol Blue (MTB) Method: An interesting method has been developed; this method is based on the catalytic action of small amounts of sulfate upon the slow reaction between zirconium and methyl thymol blue in acid solution. The method is applicable only to trace sulfate concentrations (< 2.5 ppm) because the formation of the sulfato zirconium complex begins to interfere at higher concentrations.[201]

A-IV. Methods Employing Organic Sulfates: Attempts to develop an organic reagent for selective precipitation of sulfate (as opposed to the numerous insoluble salts barium forms) dates back more than eighty years. Use of benzidine as a sulfate precipitant was suggested by Vaubel[513] before the turn of the century. Use of organic reagents can be classified as follows.

A-IV-1. Gravimetric Methods: Gravimetric methods have been suggested with benzidine,[51] 4,4'-diaminotolane,[55] 4-amino,4'-chloro biphenyl,[54] and 1,8-diaminonaphthalene.[51] Respective solubilities in mg/l at 25°C are: 98, 222, 59 and 155. All of these have solubilities that are almost two orders of magnitude higher than that of barium sulfate and as such has never been used much.

A-IV-2: Turbidimetric and Nephelometric Methods: Turbidimetric and nephelometric methods employing organic precipitants have originated largely from the university of Birmingham in the United Kingdom. This school has been a pioneering one for developing new precipitants for the sulfate ion, first led by R. A. Belcher and succeeded by W. I. Stephen. The first nephelometric method of importance was introduced by Stephen et al. in 1967

utilizing 4-amino 4'-chloro biphenyl hydrochloride as precipitant and a stabilizing medium of peptone-gum Ghatti-hydrochloric acid.[327] Later, he introduced 2-amino perimidine hydrochloride (Perimidinylammonium chloride, 2-Perimidinyl ammonium chloride, PDA-Cl) as a sulfate precipitant (solubility of the sulfate salt 20 mg/l at 18°C) and developed a sensitive mephelometric method.[469] The procedure has later been automated by others;[35] however, work done in this laboratory shows that Stephen's original method suffers extensive interferences from many anions and led to unacceptably high values. Therefore, the method may not be very useful in real determination problems.[453]

A-IV-3. Treatment of the Precipitated Sulfate: Most of the methods involving organic reagents can be classified under this category. The precipitate is filtered and washed free of excess reagent and then it is either determined by acidimetry (reaction with alkali liberates the free organic weak base from the sulfuric acid salt) or it is chemically treated to develop a color.

A-IV-3a. Acidimetry: Benzidine sulfate has been titrated with sodium hydroxide using phenolphthalein as indicator.[71] Considerable attention has been paid to the washing techniques (used to remove the excess reagent) to minimize the loss of precipitated benzidine sulfate.[25,306] Sulfate salts of 4-4'-diaminotolane,[53] 4-amino, 4'-chlorobiphenyl[54] have been similarly titrated using phenolphthalein or a mixture of phenyl red and bromothymol blue as indicator. None of these methods are any longer in use.

A-IV-3b. Development of Color by Chemical Reaction: Far more

attention has been paid to develop different colored products with the relatively reactive benzidine sulfate by reactions with various reagents and thus quantitating the amount of sulfate through colorimetry. Benzidine sulfate has been treated with a mixture of ammonia, iodine, and iodide and the resultant brown color compared with that of a standard;[539] with hydrogen peroxide and ferric chloride to produce a yellow product,[518] with an alkaline solution of β-naphthaquinone-4-sulfonic acid,[324] and with phosphotungstomolybdic acid.[279] In two step processes, benzidine sulfate has been diazotized and coupled to phenol[250] or N-(1-naphthyl) ethylenediamine[258] or thymol.[87]

In the present work 2-perimidinyl ammonium sulfate [PDA-sulfate, $(PDA)_2SO_4$] has been nitrated to produce an intensely colored product.

A-IV-4. Thermal Decomposition of Precipitated Sulfate: An interesting variation of the treatment of the precipitated organic sulfate is a recent method developed in this laboratory.[484] The method employs thermal decomposition of precipitated PDA-sulfate to sulfur dioxide. The sulfur dioxide is determined by the West-Gaeke procedure[166] or by a sulfur flame luminescence monitor. Since the pyrolytic product is characteristic of the sulfate salt, removal of excess reagent is unnecessary.

A-IV-5. Semidirect Methods. Corresponding to the methods that involve metal ion precipitants, sulfate has been precipitated by organic reagents, the precipitate was filtered off and the excess reagent was determined by spectrophotometry. Reagents

used were 4-amino, 4'-chloro diphenyl hydrochloride[244] and PDA-chloride.[75,245] One report[75] suggested the addition of the insoluble sulfate to promote nucleation. In both cases measurements were made in the ultraviolet region.

A-V. Other Methods Involving Precipitation or Formation of a Sulfate Complex: There have been only a few methods involving an insoluble sulfate or a sulfate complex other than those related to barium, lead, thorium, zirconium or organic cations.

Chronologically, mention should first be made of hexammine cobalt (III) tribromide $[Co(NH_3)_6]Br_3$ which Mahr and Krauss[320] used for precipitating the sulfate salt $[CO(NH_3)_6]\ BrSO_4$ in a gravimetric method. Following a similar study with polynuclear cobalt complexes, Belcher and Gibbons[52] introduced the historically important Werner complex, octammine-μ-amino-μ-nitro dicobalt (III) tetra nitrate, $[NH_3]_4\ Co\langle^{NH_2}_{NO_2}\rangle Co(NH_3)_4]\ (NO_3)_4$ and used it as a gravimetric reagent to precipitate the corresponding disulfate. This salt had a solubility of only 22.5 mg/l at 25°C; this solubility is far lower than that of all organic sulfates (except the recently introduced PDA-sulfate).

Both the reagents mentioned have later been used as titrants in direct conductometric procedures.[230]

Another important branch of sulfate determination has involved the iron (III)-sulfate complexes. Mention has already been made earlier of titrating this complex with barium chloride.[231] Spectrophotometric direct measurement methods have been developed based on the absorption due to this complex.[179] Another

spectrophotometric method was based on the decrease in absorbance due to the destruction of the thiocyanato-iron (III) complex by the sulfate ion.[41]

B. Other Methods: Methods Not Involving Precipitation of an Insoluble Sulfate or Formation of a Sulfato Complex.

B.1. Reduction to Sulfide: Primary among these procedures are methods which utilize reduction of the sulfate ion to sulfide and subsequent determination as such.

Of various reducing cocktails used, the following are important: hydroiodic acid, red phosphorus and formic acid[237,433]; hydroiodic acid, hypophosphorus acid and sodium acetate[188]; hydroiodic acid, sodium hypophosphite and acetic anhydride[119]; hydroiodic acid, hydrochloric acid and hypophosphorus acid[216]; and tin (II) chloride and orthophosphoric acid.[227] Reduction to sulfide has also been achieved by simply aspirating the solution into a hydrogen-rich flame.[111b]

The sulfide thus produced has been directly measured by gas chromatography as hydrogen sulfide[227] or by a sulfur flame luminescence detector.[111b] The latter method, as a whole, is not sulfate selective since the hydrogen-rich flame, used for reduction in this method, converts virtually all sulfur containing species to elemental sulfur. The sulfur luminesces as the S_2 molecule in the flame and the luminescence is measured between 300-420 nm.

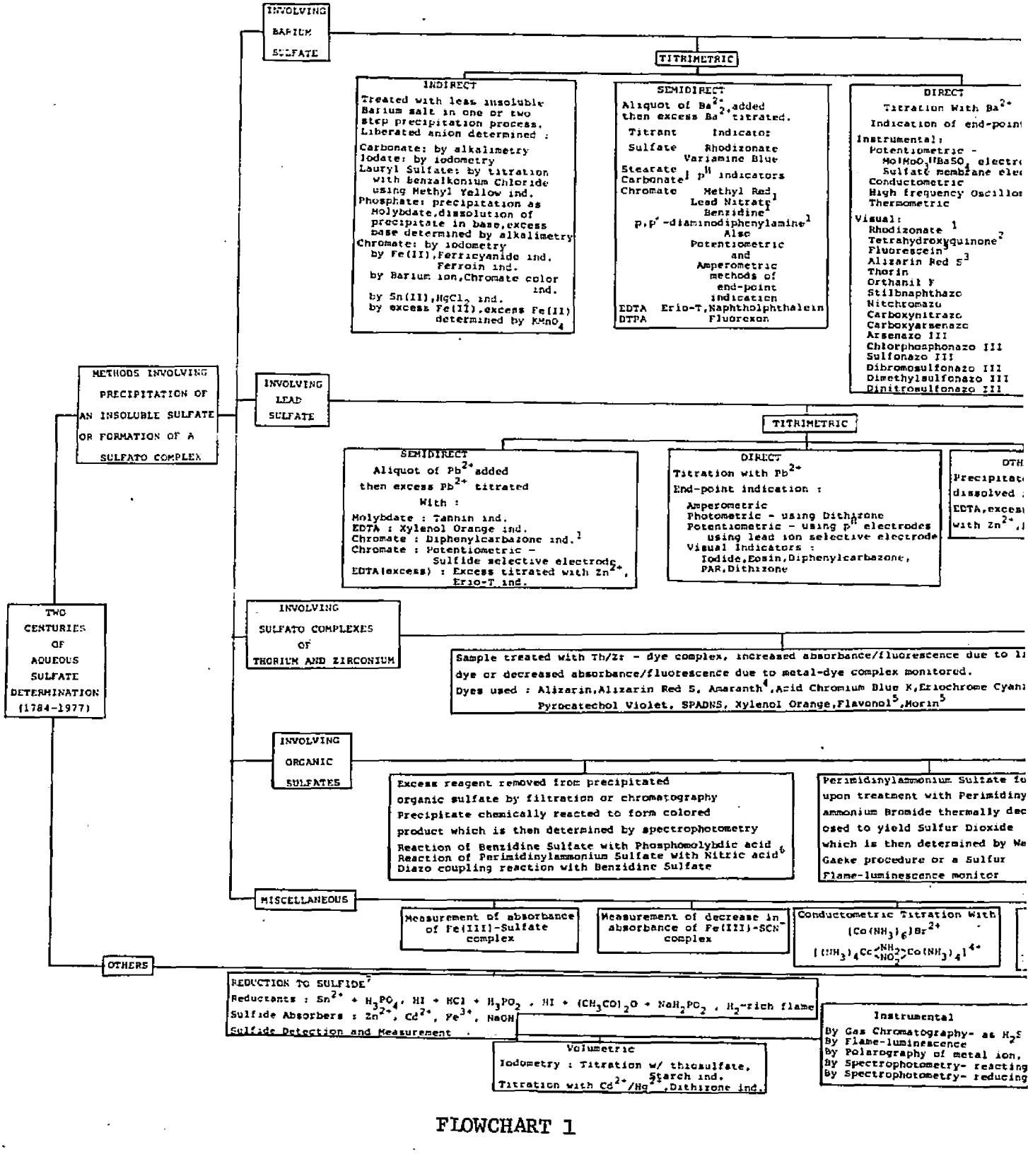
Alternatively, the liberated hydrogen sulfide has been absorbed in iodine solution containing cadmium sulfate (excess

iodine subsequently determined iodometrically)[392], or in zinc acetate[256] or cadmium[514] acetate solutions followed by an aliquot of iodine solution (excess iodine determined iodometrically); in zinc acetate solution (and then treated with an iron salt and p-amino dimethylaniline to produce methylene blue - measured colorimetrically);[188,237,433] in a buffered mixture of iron(III) and o-phenanthroline and the iron (II) complex formed measured);[119] in cadmium chloride solution (and the resulting cadmium sulfide filtered, washed, dissolved in hydrochloric acid and the cadmium ion measured polorographically);[216] and in sodium hydroxide solution containing dithizone, (then titrated with cadmium or mercuric acetate until the color of the metal dithizonate appeared).[27]

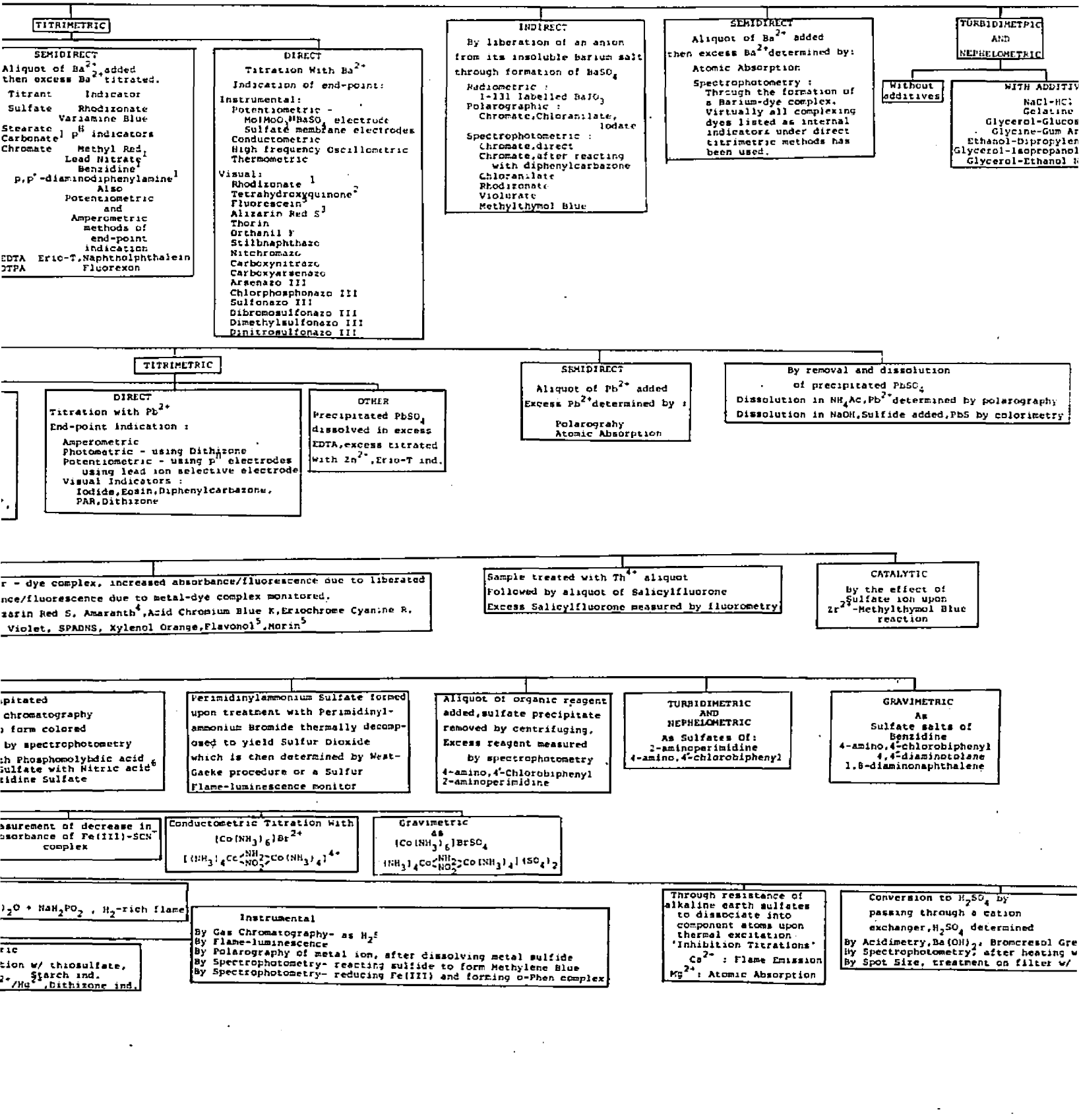
B-II. Conversion to Sulfuric Acid: In these methods, the sample is passed through a cation exchanger. Upon evaporation of the eluent, ordinary volatile acids (except phosphoric acid) are driven off, leaving sulfuric acid. The sulfuric acid is then determined. Of methods actually applied to aqueous sulfate determination, the more important means of determining this sulfuric acid residue has been: titration with barium hydroxide with bromocresol green as indicator;[131] heating with saccharose for an hour and colorimetrically determining the yellow brown color developed,[372] and a spot test on a filter with a complex silver salt, resulting finally in the formation of red silver chromate.[334] In the last method dilution of of the residual concentrate was necessary and the diameter of the silver chromate spot formed was logarithmically related to the amount of the acid.

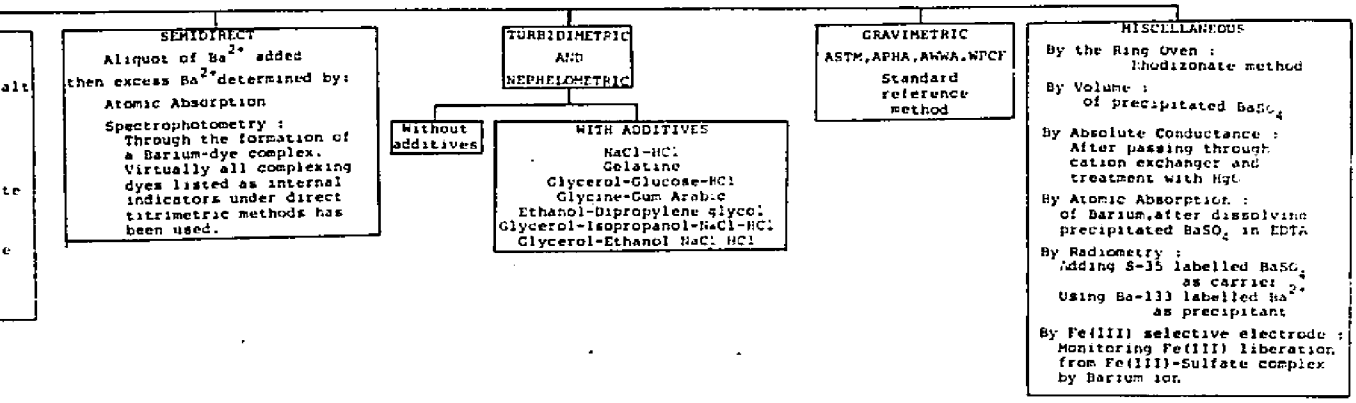
B-III. Inhibition Titrations: Inhibition titrations were introduced by Huber; these methods are based on the reluctance of alkaline earth sulfates to dissociate into component atoms upon thermal excitation. The sulfate solution was aspirated into a hydrogen-air flame while being titrated with a standard magnesium or calcium ion solution. The atomic absorption[294] or the flame emission signal[434] of the metal atom was monitored. A sudden increase in the signal indicated the end point. The method has been successfully applied to trace sulfur analysis in actual water samples.[284]

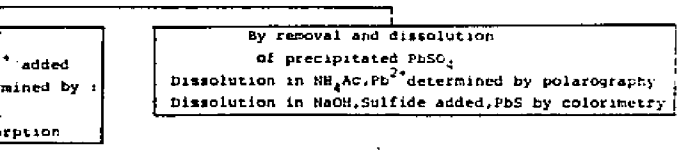
B-IV. Microbiological Determination: This is the final method to be described in this chapter and it is aptly suited to be a climactic note, since this truly involves the union of two interdisciplinary sciences. Although the applicability of such a method to real-life samples containing other ions is doubtful, Omura[373] found that the growth of the bacteria Escherichia Coli is inhibited by the sulfate ion and that the extent of inhibition is related to sulfate concentration. The growth itself can be followed turbidimetrically (after an incubation period of 8 hrs. at 35°C) and based on this principle, a turbidimetric sulfate determination method was developed.

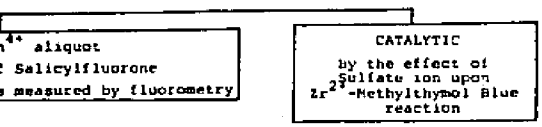

TWO CENTURIES OF AQUEOUS SULFATE DETERMINATION (1784-1977)
METHODS INVOLVING PRECIPITATION OF AN INSOLUBLE SULFATE OR FORMATION OF A SULFATO COMPLEX
INVOLVING BARIUM SULFATE
TITRIMETRIC
INDIRECT
Treated with less insoluble Barium salt in one or two step precipitation process. Liberated anion determined :
Carbonate: by alkalimetry
Iodate: by Iodometry
Lauryl Sulfate: by titration with Benzalkonium Chloride using Methyl Yellow ind.
Phosphate: precipitation as Molybdate, dissolution of precipitate in base, excess base determined by alkalimetry
Chromate: by iodometry
by Fe(II), Ferricyanide ind. Ferroin ind.
by Barium ion, Chromate color ind.
by Sn(II), HgCl2 ind.
by excess Fe(II), excess Fe(II) determined by KMnO4
SEMIDIRECT
Aliquot of Ba2+ added then excess Ba2+ titrated.
Titrant Indicator
Sulfate Rhodizonate
Variamine Blue
Stearate pH indicators
Carbonate
Chromate Methyl Red
Lead Nitrate
Benzidine
p,p'-diaminodiphenylamine
Also Potentiometric and Amperometric methods of end-point indication
EDTA Erio-T, Naphtholphthalein
DTPA Fluorexon
DIRECT
Titration With Ba2+
Indication of end-point
Instrumental:
Potentiometric - Mo|MoO3|BaSO4 electr
Sulfate membrane ele
Conductometric
High frequency Oscillo
Thermometric
Visual:
Rhodizonate
Tetrahydroxyquinone
Fluorescein
Alizarin Red S
Thorin
Orthanil F
Stilbnaphthazo
Nitchromazo
Carboxynitrazo
Carboxyarsenazo
Arsenazo III
Chlorphosphonazo III
Sulfonazo III
Dibromosulfonazo III
Dimethylsulfonazo III
Dinitrosulfonazo III
INVOLVING LEAD SULFATE
TITRIMETRIC
SEMIDIRECT
Aliquot of Pb2+ added then excess Pb2+ titrated With :
Molybdate : Tannin ind.
EDTA : Xylenol Orange ind.
Chromate : Diphenylcarbazone ind.
Chromate : Potentiometric - Sulfide selective electrode
EDTA(excess) : Excess titrated with Zn2+, Erio-T ind.
DIRECT
Titration with Pb2+
End-point indication :
Amperometric
Photometric - using Dithizone
Potentiometric - using pH electrodes using lead ion selective electrode
Visual Indicators :
Iodide, Eosin, Diphenylcarbazone, PAR, Dithizone
DTH
Precipitat
dissolved
EDTA, excess
with Zn2+,
INVOLVING SULFATO COMPLEXES OF THORIUM AND ZIRCONIUM
Sample treated with Th/Zr - dye complex, increased absorbance/fluorescence due to li
dye or decreased absorbance/fluorescence due to metal-dye complex monitored.
Dyes used : Alizarin, Alizarin Red S, Amaranth, Acid Chromium Blue K, Eriochrome Cyani
Pyrocatechol Violet, SPADNS, Xylenol Orange, Flavonol, Morin
INVOLVING ORGANIC SULFATES
Excess reagent removed from precipitated organic sulfate by filtration or chromatography
Precipitate chemically reacted to form colored product which is then determined by spectrophotometry
Reaction of Benzidine Sulfate with Phosphomolybdic acid
Reaction of Perimidinylammonium Sulfate with Nitric acid
Diazo coupling reaction with Benzidine Sulfate
Perimidinylammonium Sulfate fo
upon treatment with Perimidiny
ammonium Bromide thermally dec
osed to yield Sulfur Dioxide
which is then determined by Ne
Gaeke procedure or a Sulfur
Flame-luminescence monitor
MISCELLANEOUS
Measurement of absorbance of Fe(III)-Sulfate complex
Measurement of decrease in absorbance of Fe(III)-SCN- complex
Conductometric Titration With
(Co(NH3)6)Br2+
[(NH3)4Co(NH2,NO2)Co(NH3)4]4+
OTHERS
REDUCTION TO SULFIDE
Reductants : Sn2+ + H3PO4 , HI + HCl + H3PO2 , HI + (CH3CO)2O + NaH2PO2 , H2-rich flame
Sulfide Absorbers : Zn2+, Cd2+, Fe3+, NaOH
Sulfide Detection and Measurement
Instrumental
By Gas Chromatography- as H2S
By Flame-luminescence
By Polarography of metal ion,
By Spectrophotometry- reacting
By Spectrophotometry- reducing
Volumetric
Iodometry : Titration w/ thiosulfate, Starch ind.
Titration with Cd2+/Hg2+, Dithizone ind.

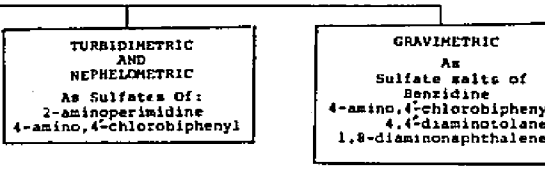
FLOWCHART 1


TITRIMETRIC
SEMIDIRECT
Aliquot of Ba2+ added then excess Ba2+ titrated.
Titrant
Indicator
Sulfate
Rhodizonate
Variamine Blue
Stearate
Carbonate
pH indicators
Chromate
Methyl Red
Lead Nitrate
Benzidine
p,p'-diaminodiphenylamine
Also Potentiometric and Amperometric methods of end-point indication
EDTA
Eriо-T, Naphtholphthalein
DTPA
Fluorexon
DIRECT
Titration With Ba2+
Indication of end-point:
Instrumental:
Potentiometric - MoIMoO4IIBaSO4 electrode
Sulfate membrane electrodes
Conductometric
High frequency Oscillometric
Thermometric
Visual:
Rhodizonate
Tetrahydroxyquinone
Fluorescein
Alizarin Red S
Thorin
Orthanil V
Stilbnaphthaze
Nitchromazo
Carboxynitrazo
Carboxyarsenazo
Arsenazo III
Chlorphosphonazo III
Sulfonazo III
Dibromosulfonazo III
Dimethylsulfonazo III
Dinitrosulfonazo III
INDIRECT
By liberation of an anion from its insoluble barium salt through formation of BaSO4
Radiometric :
1-131 labelled BaIO3
Polarographic :
Chromate, Chloranilate, Iodate
Spectrophotometric :
Chromate, direct
Chromate, after reacting with diphenylcarbazone
Chloranilate
Rhodizonate
Violurate
Methylthymol Blue
SEMIDIRECT
Aliquot of Ba2+ added then excess Ba2+ determined by:
Atomic Absorption
Spectrophotometry :
Through the formation of a Barium-dye complex. Virtually all complexing dyes listed as internal indicators under direct titrimetric methods has been used.
TURBIDIMETRIC AND NEPHELOMETRIC
Without additives
WITH ADDITIV
NaCl-HCl
Gelatine
Glycerol-Glucos
Glycine-Gum Ar
Ethanol-Dipropylen
Glycerol-Isopropanol
Glycerol-Ethanol
TITRIMETRIC
DIRECT
Titration with Pb2+
End-point Indication :
Amperometric
Photometric - using Dithizone
Potentiometric - using pH electrodes
using lead ion selective electrode
Visual Indicators :
Iodide, Eosin, Diphenylcarbazone, PAR, Dithizone
OTHER
Precipitated PbSO4 dissolved in excess EDTA, excess titrated with Zn2+, Eriо-T ind.
SEMIDIRECT
Aliquot of Pb2+ added
Excess Pb2+ determined by :
Polarograhy
Atomic Absorption
By removal and dissolution of precipitated PbSO4
Dissolution in NH4Ac, Pb2+ determined by polarography
Dissolution in NaOH, Sulfide added, PbS by colorimetry
r - dye complex, increased absorbance/fluorescence due to liberated
nce/fluorescence due to metal-dye complex monitored.
zarin Red S, Amaranth, Azid Chromium Blue K, Eriochrome Cyanine R,
Violet, SPADNS, Xylenol Orange, Flavonol, Morin
Sample treated with Th4+ aliquot
Followed by aliquot of Salicylfluorone
Excess Salicylfluorone measured by fluorometry
CATALYTIC
By the effect of Sulfate ion upon Zr2+-Methylthymol Blue reaction
pitated
chromatography
form colored
by spectrophotometry
h Phosphomolybdic acid
Sulfate with Nitric acid
idine Sulfate
Perimidinylammonium Sulfate formed upon treatment with Perimidinyl-ammonium Bromide thermally decomposed to yield Sulfur Dioxide which is then determined by West-Gaeke procedure or a Sulfur Flame-luminescence monitor
Aliquot of organic reagent added, sulfate precipitate removed by centrifuging. Excess reagent measured by spectrophotometry
4-amino, 4'-Chlorobiphenyl
2-aminoperimidine
TURBIDIMETRIC AND NEPHELOMETRIC
As Sulfates Of:
2-aminoperimidine
4-amino, 4'-chlorobiphenyl
GRAVIMETRIC
As
Sulfate salts of
Benzidine
4-amino, 4'-chlorobiphenyl
4,4'-diaminotolane
1,8-diaminonaphthalene
asurement of decrease in
sorbance of Fe(III)-SCN
complex
Conductometric Titration With
[Co(NH3)6]Br2+
[(NH3)4Co<NH2 NO2>Co(NH3)4]4+
Gravimetric
as
[Co(NH3)6]BrSO4
[(NH3)4Co<NH2 NO2>Co(NH3)4](SO4)2
)2O + NaH2PO2 , H2-rich flame
Instrumental
By Gas Chromatography- as H2S
By Flame-luminescence
By Polarography of metal ion, after dissolving metal sulfide
By Spectrophotometry- reacting sulfide to form Methylene Blue
By Spectrophotometry- reducing Fe(III) and forming o-Phen complex
Through resistance of alkaline earth sulfates to dissociate into component atoms upon thermal excitation
'Inhibition Titrations'
Ca2+ : Flame Emission
Mg2+ : Atomic Absorption
Conversion to H2SO4 by passing through a cation exchanger, H2SO4 determined
By Acidimetry, Ba(OH)2, Bromcresol Gre
By Spectrophotometry, after heating w
By Spot Size, treatment on filter w/
tion w/ thiosulfate, Starch ind.
2+/Hg2+, Dithizone ind.

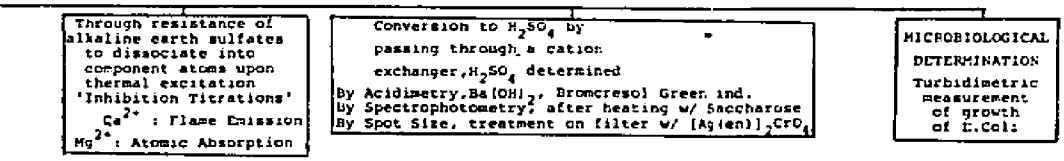








Notes:
1. External indicator
2. Used both externally and internally
3. Adsorption indicator
4. For Thorium only
5. Fluorometric finish generally used
6. This work, Ring Oven modification incl.
7. Specific for most sulfur containing species, not sulfate alone.



CHAPTER V

THE DETERMINATION OF AIRBORNE SULFATES

"Once the terrain of higher ground has been reached, we shall find many avenues leading on to the horizon. When these have been gained the journey will be more swift. It makes little difference which of these highways later we may choose; the habits of perseverance, exactness, orderliness and impartiality of judgement, which we learn as we clear these simpler approaching pathways, will be found to be the means also of surmounting obstacles as yet remote. And nowhere more than in quantitative analysis does one acquire discipline in avoiding detours; nowhere does one learn better the priceless value of assurance gained after each advance through what, a few miles back, might have appeared as a formidable tract; nowhere else does one more quickly sense with what sure success careful thought and skillful technique sweep away entanglements."

- C. W. Griffin, 1949

In this chapter the available methods for the determination of airborne sulfate salts (solid or liquid aerosols) and/or aerosol sulfuric acid will be discussed. In early work, a substantial amount of effort was made to determine total soluble sulfate (TSS) which includes both sulfuric acid and virtually all sulfate salts to be found in ambient air. Since most trace methods developed for aqueous sulfate determinations are applicable to such studies, no further discussions of such methods will be carried out here, unless the method was especially developed for and is particularly suited to ambient air analysis.

The first reported work on the determination of sulfuric acid mist in air appears to date back more than half a century[435] when a minor concern existed about the environment in or around sulfuric acid plants. Two brief reviews due to Maddalone[311] and Thomas[487] are available in their respective doctoral dissertations. The first and only review article dealing specifically with airborne sulfate analysis in ambient air is a recent publication by Tanner and Newman,[478] of Brookhaven National Laboratory. It is relatively comprehensive within its scope and highly biased. The authors have an undue fascination for the degree of complication of the method and the extent of sophistication involved in the instrumentation. This author strongly feels that one needs to be concerned about this unwelcome trend. Digital readouts in instrumentation for example, are convenient but they do not represent an advancement in either sensitivity, precision or accuracy by themselves.

I. Size Discrimination and Sampling Media

The determination of airborne sulfate is fraught with problems in both sampling and analysis stages, especially if speciation (i.e., in what form(s) the sulfate exists) is to be carried out. Speciation is generally necessary for hazard evaluation because the toxicity of the acid aerosol and its various salts vary markedly. By the same token, aerosol sizing is necessary because health effects are very dependent on particle size. Use of the Andersen cascade impactor,[19,420,517] Goetz aerosol analyzer,[178,295-7] Lundgren impactor,[26,298,300,525] and other highly specialized sampling trains[123,325,411] has been made for size classification and subsequent analysis. Further details are beyond the scope of this discussion.

Sampling by Filtration

The filter material used for sampling has been subject to much research. An unsolved problem using high volume samplers remains due to the conversion of sulfur dioxide to sulfate catalytically at the surface of certain particulates, namely metallic compounds. Presumably, the process occurs via chemisorption. In addition, some filter media, especially galss fiber, have a high capacity to absorb sulfur dioxide[36,81] and may even contain reactive oxidation sites themselves, capable of converting sulfur dioxide to sulfate.[58] Results of studies on some available brands have been reported.[274]

In situations where sulfur dioxide loading of the air is two orders of magnitude higher than the aerosol sulfuric acid content

(as is often the case), the conversion of sulfur dioxide to sulfate can become a real problem with high volume samplers, (which is necessitated because of the rather small sulfuric acid content of the ambient air - average urban background generally is $\sim 10\ \mu g/m^3$) leading to serious errors. For this reason attempts have been made[142] to "diffusion denude" the sample stream of ammonia and sulfur dioxide, before sampling. The method however, is unproven and complicated and therefore not in general use. It is generally agreed[478] that the best way to reduce collected particle induced sulfur dioxide to sulfate conversion is by collecting as little sample as possible. This also provides a more representative sample of the material actually present in the ambient atmosphere because interparticle collision induced interactions are reduced.

The use of high purity quartz filters has only recently been introduced for airborne sulfate sampling.[30,477] Ordinary paper filters (such as Whatman, Nos. 1, 4, 41 etc.) are generally no longer used in sulfuric acid sampling. Other than glass fiber filters, polytetrafluoroethylene (PTFE) filters (such as Fluoropore, Mitex, etc.) have also been frequently used. Sampling efficiency of these filters for aerosol sulfuric acid may, however, be quite low.[417] Another problem associated with submicron pore size PTFE filters is the high pressure drop across the filter making them generally unsuited for high volume sampling.

On the other hand, both glass fiber and paper filters contain reactive alkaline sites that neutralize the collected acid aerosol

and thus lead to unacceptably low results if acidimetric methods are used for analysis. While repeated washing apparently makes paper filters usable, general pretreatment does not remove all alkaline sites from a glass fiber filter.[126] Use of membrane filters (cellulose acetate, polycarbonate, etc.) have been reported[381] but they suffer from the same problem of neutralization; in these cases through esterification. With glass fiber filters, residual alkali content of the filter may lead up to 8 μg sulfuric acid loss/cm^2 of filter,[438] and may also contain high residual sulfate.[159] Drastic pretreatment procedures have been suggested;[44,56] It should be noted that regardless of pretreatment all filter media are not compatible with all types of analytical finishes. Higher purity glass fiber filters have recently become available;[170] the residual sulfate content of these filters is quite small although the number of alkaline sites in the filters is still prohibitively high for acidimetric measurements to be meaningful. It is believed, however, that in actual field samples, neutralization of the acid aerosol is probably far less than observed in laboratory studies. The reasons are believed to be: a) sulfur dioxide saturation of the alkaline sites[438] and b) inability of liquid sulfuric acid droplets to penetrate into the filter media.[311] Dubois, et al.[139] have given an interesting discussion of why the amount of acid aerosol determined is not linear with the volume sampled.

There are only a few reported methods which use chemically impregnated filters that immobilize the acid aerosol by reaction

at the moment of its collection. This work utilizes such a technique. There are a number of inherent advantages with the use of an impregnated filter. Glass fiber filters, which are most commonly used, are generally quite efficient collectors of aerosol sulfuric acid. It has been shown however, that at very low levels loss occurs through the evaporation of acid aerosol; and at high levels, some acid may flow through the filter.[480] These problems are obviated with an impregnated filter that immediately reacts with the acid aerosols.

Also, loss of acid through undesired neutralization by simultaneously collected basic particulate matter or by the omnipresent gaseous ammonia in the sample stream or by the alkaline sites in the filter itself, no longer poses a problem.

As an example of the more unusual media used for filters, graphite[526] may be cited. The use of most other filter media, such as cotton or combinations of cotton with other material,[7,176,390,441] asbestos,[98,403] sintered glass[156,181] and alundum[481] may be regarded as historical, as far as ambient air monitoring is concerned. Some of these materials are still in use in monitoring air quality in sulfuric acid plants. Specially formulated cellulose fiber mats have been used for high altitude high velocity sampling[467] in the stratosphere and polystyrene filters have also been tried for stratospheric sampling.[271]

Sampling by Other Techniques: Sampling by techniques other than filtration consist of absorption in a liquid[37,108,127,185,239,318,399,435,441,468] (the absorber being water or water-containing

alkali or surfactants) which makes at best only a determination of total soluble sulfate possible; electrostatic precipitation,[29,133,439] sonic agglomeration,[117,432] adsorption on various material (such as charcoal, calcium chloride, pumice, etc.)[398,435] and impaction.[112,181,321,393] Of these, only impaction techniques are still in general use. Filtration itself in fact may be considered to be an impaction technique. Impaction techniques not involving filtration are generally carried out on chemically pretreated surfaces, microscopy being the common method of evaluation. Modern size discriminating impactors have been referred to earlier in this Chapter.

II. ANALYSIS

The determination of total airborne sulfate is often carried out by techniques that are atom-selective, and this is permissible only because most of the airborne sulfur is in the form of sulfate.[158] Needless to say, these techniques do not distinguish between the various sulfate species and sulfuric acid or non-sulfate sulfur. Applicability of such results to environmental hazard evaluations is therefore highly questionalbe and justify only briefly mention.

Total soluble sulfate (TSS) determination, by the same token, is not a good measure of hazard index. Many trace techniques mentioned in the previous chapter have been applied and some specifically developed for airborne sulfate analysis.

All techniques that use liquid absorbers necessarily have to determine total soluble sulfate or net acidity. In either case, serious errors are caused by simultaneous absorption of sulfur

dioxide and its subsequent oxidation. Sulfur dioxide is oxidized quantitatively to sulfuric acid in the presence of certain metal ions.[308] In some methods[147] that use a liquid absorber, an oxidizing absorbent (e.g., hydrogen peroxide) is intentionally used to convert the sulfur dioxide to sulfuric acid quantitatively. The sulfur dioxide is also determined separately and subtracted from the total sulfate obtained by the first procedure. Methods such as conductometric measurements, which were developed for sulfuric acid plant exit gas analysis, are inadequate for airborne sulfate determination and will not be discussed. It should also be noted that repeated leaching with water do not remove all ionic sulfate from many of the filter media, especially glass fiber,[159] because of its adsorption characteristics and inability of water to wet the material.

Determination of acidity of the collected sample possibly is a better index of aerosol sulfuric acid content than total soluble sulfate values. It is generally agreed that sulfuric acid is the main contributor ot atmospheric acidity, a conclusion that is substantiated by analyses of acid rain.[283] In actual sampling situations however, even if errors due to the presence of other acids is neglected, neutralization through various routes are likely to cause large indeterminate errors.

Methods that can differentiate between sulfuric acid and its salts are environmentally the most meaningful. Such methods can be classified under two categories:

a) methods that depend on direct instrumental speciation, and

b) methods that use a physical or chemical treatment to speciate.

A more detailed discussion of the various analytical processes now follows; a flow chart of the available methods is attached at the end of this chapter.

A. METHODS DETERMINING TOTAL AEROSOL SULFUR

X-Ray fluorescence analysis (XRFA) measure x-rays emitted from sulfur, induced by x-rays[182] or protons and other charged particles.[107] Extensive data on total aerosol sulfur obtained by XRFA have been reported by Dzubay, et al.[143b]

X-Ray photoelectron spectroscopy (XPES, also called ESCA) has been extensively employed by Novakov, et al.[109,363-4] to speciate various different oxidation states of sulfur in aerosols. It is at best semi-quantitative and assignment of different photoelectron energies is often ambiguous.

Both XPES and XRFA are basically surface studies, and may not provide true composition of the total sample, especially due to high surface loading of adsorbed sulfur dioxide on the filter. X-Ray fluorescence analysis may also be subject to interference from lead, which has overlapping fluorescent energies. Reportedly, Raman spectroscopy has also been used for characterization, but quantitative estimation is still impossible.[421] X-Ray diffraction can be used as an auxilliary technique to qualitatively identify solid particulate material.[69] It does not, however, reveal the presence of the species of main interest, i.e., sulfuric acid.

The flame photometric detector (FPD)[111a,b] can be used to directly monitor aerosol sulfur loading. Sulfur dioxide must first

be removed and this has been accomplished by laminar flow through tubes which has their inside walls coated with some sulfur dioxide absorbers.[142] Alternatively filtered and non-filtered sample streams have been monitored. The filtered sample is assumed to contain no particulates and the difference therefore gives the aerosol sulfur loading.[111a] The response of the FPD however, is dependent on the chemical nature of the aerosol sulfur, even the physical form of the aeresol sulfate.[220] Also sensitivity must be improved in commercially available instruments if they are to be used for direct monitoring of ambient air. Roberts and Friedlander[410] have used the FPD to determine aerosol sulfur by heating the collected sample to $\sim$ 1100°C through capacitive discharge.

Exciting possibilities exist for determining total aerosol sulfur by atomic absorption through the heated graphite atomizer (HGA) and the new sulfur lamp emitting in far-uv.[301]

B. METHODS DETERMINING TOTAL SOLUBLE SULFATE

A review of sensitive methods for determining the sulfate ion that can be applied to airborne sulfate analysis has been compiled by Hoffer and Kothny.[207] Barium sulfate turbidimetry is still popular but possibly the most frequently used method is the automated methyl thymol blue procedure[2,310] in spite of the fact that removal of all interfering cations by ion exchange constitute an unwelcome necessity. The same is true for another popular method that involves microtitration with barium perchlorate using thorin indicator and in which visual or spectrophotometric means

of end point detection are employed.[380,418] Spectrophotometric methods using barium chloranilate and the barium nitrochromeazo dye complex are in use.[207] Dimethylsulfonazo III is reportedly the best indicator for direct titrations.[448] Removal of interfering cations is again a necessity in all of these methods. Methods that determine excess lead or barium after precipitation of the corresponding sulfate have been devised but are not popular. X-Ray fluorescense of barium after precipitating barium sulfate has been used,[88] and an indirect chromate method has been developed to measure excess chromate by square-wave polarography.[137] Reduction to hydrogen sulfide and determination by the iron (II)-phenanthroline complex through reduction of iron (III) has been applied.[119]

Alternatively the hydrogen sulfide has been determined by microcoulometry[295] or by precipitation as radioactive silver sulfide using Ag-110 tagged silver nitrate and counting the precipitate activity.[478]

Hussar, et al.[221-2] modified Roberts and Friedlander's technique of flash volatilization to total soluble sulfate (TSS) determination. Excellent sensitivities were reported.

A very unusual procedure has been reported to determine TSS. The method consists of adding an aliquot amount of excess sodium ion to the leached sample and then the excess sodium is determined by the copper complex of EDTA using pyridyl azonaphthol as an indicator. The titration is carried out in a partially aqueous medium.[387]

Use of barium rhodizonate impregnated filters has been suggested for determining aerosol sulfuric acid.[171] The barium rhodizonate is discolored and evaluation can be made by comparison with standards. Actually the method determines the total sulfate content present as liquid aerosol.

C. METHODS DETERMINING ACIDITY

Acidity is generally determined by either a measurement of pH or by acidimetric titration. Junge and Scheich in their classic paper[249] compared the pH measurement method with titrimetric procedures. If the decrease in pH from blank values is taken as the measure of free sulfuric acid concentration, results obtained may be up to a factor of 30 lower than that determined by titration to blank pH values. Beyond a doubt this is due to neutralization of the free acid by weak bases, such as ammonia and some organic bases. Interestingly enough, in highly industrialized urban atmospheres such as London, the difference in acid concentration determined by the two methods is very small. Apparently this data indicates that little or no neutralization of the free acid takes place in such atmospheres. This data also shows a good correlation between total sulfate and free acid concentration.

The first significant method for determining aerosol acidity was that reported by Coste and Courier.[108] Some idea of the method used for sulfuric acid loading of such atmospheres may be obtained from their collection procedure. They saturated the sample stream with water vapor and then passed it through an ice-cooled flask. The aerosol sulfuric acid served as condensation

nuclei and the condensate was collected. They measured pH as an index of acidity. Needless to say, the sampling process was tediously long and slow.

The next important publication was by Mader, et al.[316] and came a decade and a half later. Whatman filter papers were washed with deionized water until the pH of the leach solutions were constant within $\pm$ 0.03 units. These were dried, used for sampling and subsequently macerated with an aliquot of water and the pH measured. These investigators were the first to note that sulfuric acid content of urban ambient air (Los Angeles and London) had a correlation with fog.

About another decade and a half later, Commins[106] published a titrimetric method to determine acidity. Noting that direct titration with base yield unusually low results, he extracted the filter with a known excess of sodium tetraborate solution to prevent the acid particles from reacting with insoluble basic material. The resulting solution was then back titrated with 0.01 N H_2SO_4 with bromthymol blue as indicator which changed color at about pH 7. A few years later Persson[381] reported a method of titrating the collected sample with base to pH 5 to get "strong acids" and to pH 7 to get total acid.

In recent years Brosset and his coworkers[69] in Sweden have extensively studied and improved microtitrimetric procedures for determining acidity. They have also shown that with the aid of supplementary analyses, valuable insight to atmospheric particulate concentrations can be gained from total acidity measurement. They

applied the Gran titration techniques[183] (plotting the data as $10^{-EF/RT}$ vs. volume base; E = millivolts, F = Faradaic constant, R = Gas Constant, T = temperature in ^{o}K) and using a pH 4 leach solution they were able to reach a LOD (limit of detection) of 5 μg H_2SO_4 in a volume of 5 ml.[31] Later the method was semiautomated by generating the hydroxyl ion coulometrically and by using an exponential function generator to directly record the Gran-titration plot.[32] In a paper presented at an ACS meeting five years ago Brosset[68] commented that he regards the problem of determining strong acid content of acid aerosols as solved.

Apparently Brosset's complacence was not shared by other workers. In the very next ACS meeting, Dzubay, et al.[143a] presented an involved method for continuous monitoring for aerosol acidity using a modified NOx chemiluminescence detector. The instrument samples air for 18 minutes, stores the air in a chamber and lets in a controlled amount of ammonia from a permeation tube. Ammonia reacts with the sulfuric acid aerosol to form ammonium sulfate aerosol. The air sample is then filtered to remove the aerosol content and the excess ammonia is passed over heated copper wool at 800°C (substituted by Gold wool at 1000°C in a subsequent publication). The ammonia is thus converted to nitric oxide which is measured by a chemiluminescence detector. For the next 18 minutes the instrument goes through the same process except that the ammonia addition step is omitted. This determines the blank value. The instrument is automated to repeat the cycles.

It is doubtful how useful this method would be to measure

ambient acid aerosol levels, since the NOx monitors still do not have sufficient sensitivity. Moreover, a complete neutralization of the acid content is assumed, which may or may not be a valid assumption depending on the type of aerosol loading encountered. Neutralization may also be a function of humidity because humidity governs whether the bisulfate salts are present in a solid state or in a liquid solution. A detailed discussion of this aspect is given later in this chapter.

Two novel methods were developed in this laboratory for determining acidity. The first one[526] was a spectrophotometric procedure and employed a solution of bromophenol blue to leach the acid off the filter. The displacement of the indicator equilibrium between the dissociated and non-dissociated form was measured by noting the decrease in absorbance at 587 nm due to the ionized form.

The second method[527] was developed at the same time and this was based on a ring oven technique. After removal of the volatile acids by heating, the filter was placed at the center of a ring oven and spotted with potassium bromide solution which was then washed to the ring zone. Next, an aliquot of sodium fluorescein solution was spotted and washed to the ring zone. Potassium bromate was next added encircling the outer periphery of the ring. Bromine, which was liberated by the bromate - bromide - proton reaction reacted with sodium fluorescein to produce eosin. The intensity of the color was then compared with standards.

Use of an indicator-impregnated filter has been patented for

the determination of aerosol acidity.[359] The acidity was determined by comparison with standards. Johnstone and Gerhard[172] developed an involved method with a filter impregnated with thymol blue which turns yellow with acid. A colorimeter measured the intensity of the yellow spot through a low power microscope. The same technique was used later by Waller[520] to monitor London air.

In a recent publication Huygen[224] reported a method that involves fixation of the acid aerosol after its collection. After sample collection the filter was treated with diethylamine vapor whence the diethylamine reacted with the acid aerosol forming a salt. Excess diethylamine was then evaporated by blowing air through the filter.

The bound diethylamine was then determined spectrophotometrically by first leaching with carbon disulfide to produce diethyldithiocarbamate which was then reacted with cupric chloride to produce the copper diethyldithiocarbamate complex.[505] Interferences were reported due to binding of diethylamine by weak acids such as ammonium sulfate unless the diethylamine vapor was absolutely dry. Also, adsorption binding of the highly polar diethylamine to attendant particulate matter could be expected to cause serious errors.

Finally, a spectrophotometric method has been described that claims to measure sulfuric acid specifically but actually measures acidity. Air sample is drawn through an aliquot of water, which is then treated with ammonium vanadate solution. Formation of polyvanadates at low pH results in a yellow color which is

measured. The method suffers from interference due to various anions.

D. METHODS DETERMINING AEROSOL SULFURIC ACID

I. Instrumental Speciation: As of this writing, all instrumental techniques capable of differentiating sulfuric acid from its salts that have been developed are semiquantitative at best. Automated gas chromatographs interfaced with microcoulometric or flame photometric detectors have finally been developed for the rapid determination of hydrogen sulfide, sulfur dioxide and organic sulfur compounds[382,471] but sulfuric acid is too reactive to elute from a gas chromatographic column without reacting.

Reportedly, using some new sophisticated instrumental techniques it may be possible to determine sulfuric acid aerosol specifically. These methods are awaiting further developments. They include: plasma source emission spectroscopy,[1] molecular correlation spectroscopy[530] (also referred to as mask or D^2 spectroscopy, so called because a mask specially fabricated for a particular compound electromechanically generates the second derivative of transmittance vs. wavelength), photoionization mass spectrometry,[134] infrared laser atmosphere monitoring system (ILAMS),[463] Remote Raman system (RRS) (using a uv-laser to stimulate Raman Scatter from airborne particulates),[476] long path infrared analysis,[470] and electron microprobe analysis (also called the scanning electron microprobe, SEM).[6,57] Not a single one of the above methods is likely to become a choice method for aerosol sulfuric acid in the immediate future.

Infrared spectrometry has been used[62-3] to determine both ammonium and sulfate ions. Samples collected in different stages of a cascade impactor were made up into KBr pellets. In urban samples the bands attributed to NH_4^+ and $SO_4^=$ were present principally in the submicron size fraction and they were absent in samples collected in a desert. Later, Cunningham and his group[114] vastly improved the sensitivity and resolution by applying Fourier transformation to process the signal, developing what is now called Fourier Transform Infrared Spectroscopy (FTIR). Both accumulation time and analysis time have been drastically reduced. Potassium bromide pellet spectra were obtained for size fractionated samples from 400-3600 cm^{-1}. The bands at 1400 and 3140 cm^{-1} have been assigned to the ammonium ion and those at 1110 and 620 cm^{-1} to the sulfate ion. The method was applied[115] for continuous monitoring (3 hr. samples) during a recent pollution episode (Chicago, 1973). The complexity of the spectra with the appearance of several other bands made complete interpretation impossible. Some bands were assigned to species that are "more acidic than bisulfate" according to the authors. The complexity of the spectra is not unexpected since complex species such as $(NH_4)_3H(SO_4)_2$ (lectovicite) are established constitutents of atmospheric aerosols.[69] An integrated "sulfate acidity index" as proposed by Cunningham is therefore of questionable utility.

Direct instrumental speciation has so far been dominated by electron or optical microscopic techniques. Electron microscopic identification of ammonium sulfate aerosol has been

reported by Heard and Wiffen.[199] Lodge and his coworkers, by far the most active group in this field of research, have described optical and electron microscopic identification of different sulfate species collected on various media. Chemical reactions (e.g., with lead nitrate) are often used prior to microscopic examination. Lodge's first technique was to use gelatin-barium chloride-glycerol as a substrate[288] to be superceded by millipore filters[287] and then by a substrate containing barium chloride and slightly alkaline bromophenol blue.[290] In the last case, sulfate spots appeared white in a blue background, sulfuric acid spots appeared turbid yellow and other acid spots appeared yellow but not turbid. Later they proposed the use of barium rhodizonate impregnated millipore filters.[291] Anyz[23-4] has reported however, that gelatin substrates impregnated by a different method yield clearer and faster developments than the above substrates. A chemically specific microscopic method using a methylenedisalicyclic acid impregnated nitrocellulose substrate(based on Fiegl's original spot test) has been reported.[125] The plates are heated after sample collection, and red spots are produced at the acid aerosol impaction sites. Reinhart[396] incorporated barium chloride in a polyvinyl alcohol-glycerol substrate containing a trace of Triton-X-100.

In all of the above cases characteristic patterns due to a particular species appear; these are called Liesegang rings. In the case of sulfuric acid particles, a unique pattern of a central spot surrounded by satellite drops of graded sizes are

observed.[293,520] Ammonium sulfate on the other hand, yields a distinctly different type of spot. It must be remembered that microscopic analysis relies on the assumption that individual aerosol particles in the atmosphere are chemically pure species, an assumption that is unproven but generally regarded to be valid. The original particle size and total amounts are estimated using statistical techniques developed by Lodge.[289]

In a very impressive and extensive investigation using electron microscopy an Australian research team[60] has shown the superiority of thin evaporated copper films as substrates in the study of particulate sulfates and aerosol sulfuric acid. They have also investigated other substrates such as carbon and films of barium chloride, benzidine and silver nitrate. In all cases, sulfuric acid droplets produce spot patterns that are uniquely different from ammonium sulfate and other material. The interested reader is referred to the original article containing a series of excellent electron photomicrographs. Copper film having a thickness around 50 A has been recommended to be the best for these purposes. Varying film thicknesses yield slightly different but still unique spot patterns. Earlier, impaction on evaporated iron film was reported[215] and a quantitation method with a combination microscopy-photocolorimetric technique was developed.

Two other interesting results came out of the Australian study. Even within the span of the study (1968-1973) an increase in sulfuric acid content of the stratosphere was observed, and

the last set of measured values were certainly much higher than the available data indicated for 1961. Also, from samples collected over Wyoming, U.S.A., they reported their failure to detect ammonium persulfate at altitudes over 15 Km, although it was still detectible in the lower edges of the stratosphere. In an earlier study (1966)[161] over the same location, ammonium persulfate was shown to be an important constituent. In fact, it is generally regarded to be a significant constituent of the continental statospheric aerosol mass.

This information is important when viewed in the light of the fluorocarbon-ozone controversy. Ammonium persulfate is formed supposedly through a slow reaction between ammonium sulfate and/or sulfuric acid and ozone. These data would indicate that while airborne sulfate content is increasing in the lower stratosphere the ozone content in the upper stratosphere is decreasing.

Another instrumental method of doubtful specificity determines aerosol sulfuric acid.[472] Polycarbonate film is used as an impaction surface which is etched with sodium hydroxide after sampling. Apparently holes are etched where sulfuric acid droplets are impacted. The film is then used as the dielectric material of a capacitor and when voltage is applied across the capacitor terminals sparking occurs. The number of sparks is proportional to the number of holes and therefore to sulfuric acid content. Although laboratory studies seem to work, it is highly probable that variation in particle size would affect the operation of the

spark replica counter. Furthermore, nothing is known about how various other airborne particulate material may affect the polycarbonate film.

A novel and highly controversial approach to continuous monitoring has been described by Charlson, et al.,[94] utilizing a rather sophisticated instrument called the humidograph.[80] Although the method is semiquantitative at best, it will be discussed in some detail because certain insights gained from the work of these authors have been used in the present work, to be described later.

The apparatus may be described as a double beam nephelometer which measured the light scattering co-efficient (b_{sp}) in both the reference and sample compartments and electronically yielded the sample - reference quotient. An aliquot of air sample was heated first to 10-20°C above ambient temperature to reduce relative humidity (R.H.) to ca. 30% or below and then divided into the reference and the sample cells. The sample cell was provided with controlled inlets of water vapor to vary the humidity continuously which was monitored through two independent sensors, temperature and dewpoint. Both the compartments were equipped with a controlled ammonia inlet.

When $\frac{b_{sp} \text{ as a function of R.H.}}{b_{sp} \text{ at } 30\% \text{ R.H.}}$ was plotted against R.H. (the plot is called a humidogram), inflection points were observed on an otherwise relatively flat curve if deliquescent compounds were present as aerosols. These inflection points appeared at relative humidity values characteristic of each compound.

These values, of course, were nothing other than the relative humidity values corresponding to the vapor pressures associated with a saturated solution of particular salts at particular temperatures. Below this relative humidity the salt remained a dry particulate and as the humidity was raised and exceeded this value, it grew suddently into a droplet; thus, the sudden increase in the b_{sp} quotient and the inflection point on the curve. Past the inflection point the curve again rose monotonically. Since both sulfuric acid and ammonium bisulfate are highly hygroscopic, they gave rise to montonically rising humidograms.

A humidogram was taken again, after ammonia addition. The four different categories of humidograms observed by Charlson were:

a) monotonic before NH_3 addition, NH_3 caused an inflection at $\sim$ 80% R.H.

b) inflection present at $\sim$ 80% R.H. enhanced by NH_3 addition

c) inflection present at $\sim$ 80% R.H. no change with NH_3 addition

d) monotonically rising curve unaffected by NH_3.

The method as such cannot distinguish between ammonium bisulfate and sulfuric acid and they were referred to together as 'acid sulfates.' Noting that at least 30-50% of the total aerosol loading must be ammonium sulfate for a perceptible inflection point the above categories then represent in respective order: aerosol dominated by acid sulfate species, aerosol dominated by both ammonium sulfate and acid sulfate species, aerosol dominated by ammonium sulfate, and aerosol not dominated by

ammonium or acid sulfates.

While the first two conclusions are readily intelligible the second two, in this author's opinion, are not so obvious, and these were characteristic of urban samples obtained near the St. Louis area. For the third case it is possible (admittedly unlikely) for material other than ammonium sulfate to cause an inflection point and for both the third and fourth cases there is a distinct possibility that the acid sulfate did not react with ammonia, especially in view of Junge and Scheich's classic work[249] where they showed that acid aerosol particles were quite stable even in the presence of excess ammonia. They had concluded that the aerosol particles are protected by an oil film or some other organic material; a very locigal conclusion when principal sources of urban aerosol sulfur are considered. On the other hand, it is possible that the rural background results primarily from long range transport of sulfur dioxide and its oxidation.

Charlson concluded that there is no significant increase in aerosol ammonium sulfate or acid sulfate content in going from rural to urban atmosphere. Charlson's conclusions therefore become subject to proof by alternative methods. To account for the apparent coexistence of free ammonia and acid sulfates, in a very recent publication Lau and Charlson[269] have proposed that the actual ammonia concentrations are less than measured values.

Concentrations of the total ammonium sulfate and acid sulfate species has been calculated by Charlson, et al.[95] from the absolute value of the scattering coefficient. They have also

carried out an aerosol phase titration. Ammonia was added until the first inflection point appeared on the humidogram and further ammonia was added until there was no further enhancement of the inflection. From the two "end points" respective values of ammonium bisulfate and sulfuric acid can be obtained. The appearance of an inflection point at R.H. 60-65% has been observed in some urban samples, the authors concluded that it may be due to the $(NH_4)_3 H(SO_4)_2$ (letovicite) phase.

In the present author's opinion, although Charlson's work represents a very valuable contribution towards the understanding of physico-chemical behavior of atmospheric sulfates and towards an entirely new approach to their determination, the applicability of the method is highly questionable. Even disregarding the complexity and possible cost of fabricating such an instrument commercially, the method would not work unless the ammonium/acid sulfate content is at least 30-50% of the total aerosol loading. Also, b_{sp} is a highly particle size governed parameter, dominantly controlled by the particles in the 0.1-1 μ size. The authors justified this by stating that fortunately products of gas to particle conversion (chiefly oxidation of sulfur dioxide) accumulate in this size range. Junge and Scheich on the other hand, categorically state, on the basis of urban measurements, that while indeed the main mass ($\sim$ 90%) of the aerosol loading is in the 0.1 μm class, virtually the entire content of free H^+ is in the Aitken (< 0.1 μ) range. This would make Charlson's conclusions regarding urban atmospheres further subject to verification.

Also, whether neutralization of the acid aerosol actually occurs during ammonia addition with the urban samples remains to be answered.

II. METHODS INVOLVING PHYSICAL OR CHEMICAL SEPARATION

Thermal Separation: Thermal speciation involves two main techniques: volatilization/microdiffusion and pyrolysis.

Scaringelli and Rehme[438] introduced the first pyrolysis technique in 1969. The collected sample was pyrolyzed at 400°C in a nitrogen stream and the liberated sulfur trioxide was passed over heated copper where it was reduced to sulfur dioxide. The sulfur dioxide was determined by colorimetry, microcoulometry or flame photometry. The sensitivities reported were 0.3 μg, 0.03 μg, and 0.003 μg respectively. The selectivity was found to vary in the opposite order. Thermally stable collection media (e.g., glass fiber or quartz filters) were required. The method separated sulfuric acid from its metal salts, but since both ammonium sulfate and bisulfate decompose at the pyrolysis temperature, they interfered positively.

In a more recent report other workers[394] have attempted to simplify Scarringelli and Rehme's process by direct impaction on copper with subsequent thermal reduction to sulfur dioxide. Ammonium sulfate and bisulfate of course, still interfered.

In the same year, Dubois, Monkman, et al.[137] introduced their microdiffusion technique. The air sample was filtered through a glass fiber sheet and an aliquot disc was cut out of the sheet. The disc was placed inside a petri dish which was covered with

another petri dish coated inside with sodium hydroxide. The assembly was placed inside a nitrogen flushed oven at 195°C overnight during which period the sulfuric acid volatilized from the filter and was immobilized by the base. The immobilized sulfate was subsequently determined by barium perchlorate microtitration with thorin as indicator, after passing through an ion-exchange column. Again this method could not distinguish between sulfuric acid and its ammonium salts, since they also microdiffuse under the same conditions. The method has been described as a part of a general method of high volume air sample analysis in a later publication[138] and was applied to determine the sulfuric acid content of soot by the same group.[140]

It is interesting to examine the explanations offered by the two groups regarding ammonium sulfate interference. While Scaringelli and Rehme stated that they did not consider it to be a serious interference "because this compound forms in the atmosphere from sulfuric acid and gaseous ammonia", Dubois, Monkman, et al. did not even mention the word interference due to ammonium sulfate in their various papers (in fact, ammonium sulfate was used as a calibration standard) and went on to state that "the major constituent of particulate sulfate is calcium sulfate, in the form of gypsum."[137] Scaringnelli's statement was a rationalization rather than an explanation. This author has also failed to uncover any evidence in the literature which substantiated Dubois's statement regarding the general preponderance of calcium sulfate in airborne sulfate.

Another disturbing item appeared from Dubois, et al.'s first publication regarding the microdiffusion method. Justifiably they condemned the available direct acidity determination methods as being nonspecific, albeit with undue sarcasm. Then they went on to state their only assumption was that the aerosol sulfuric acid was collected quantitatively on glass fiber filters. This again, as shown by later studies,[170] was a valid assumption.

There was another underlying assumption that the authors did not recongize. This was the assumption that the collected acid was quantitatively microdiffused on to the sodium hydroxide from the glass fiber filter. Using S-35 tagged sulfuric acid and radiochemical measurements Maddalone, et al.[312] showed that even after drastic pretreatments very little, if any, sulfuric acid microdiffuses from a glass fiber filter. Even with the most drastic treatment (the filter soaked in 20% sulfuric acid for 3 days, then boiled for 10 minutes then rinsed in water, 80% isopropanol, and acetone to remove the excess acid and then air dried (Barton and McAdie)[44] only 4% of the sulfuric acid put on the filter was recovered after a 24-hr. microdiffusion.
(This represented an improvement of a factor of more than 100 over that of untreated filters - recovery 0.034%!)

Since both Scarringelli and Rheme's and Dubois, et al.'s method included the ammonium salts with the acid aerosol, on retrospect it becomes understandable why the ratio of aerosol sulfuric acid (plus ammonium salts)/total sulfate in actual ambient samples was observed to be almost an order of magnitude

lower by the second group. What Dubois, et al. actually microdiffused was probably the ammonium salt rather than the acid itself which was far more tightly bound to the filter. Indeed this would also explain their choice to use ammonium sulfate, rather than the acid, as the calibration standard.

Maddalone, et al.'s[312] extensive investigation covered a number of other media, such as polytetrafluoroethylene (PTFE), graphite, paper, and Nucleopore and Solvinert filters. The highest recoveries were obtained with the first two materials and very little with the rest. A detailed discussion of optimization of other variables such as filter size vs. petri dish diameter, unpolished vs. polished edges of a petri dish, and period of diffusion was given in Maddalone's excellent dissertation. The maximum recovery that he observed was $\sim 85\%$ from PTFE and graphite filters.

Although according to reported data in the literature, decomposition of ammonium sulfate does not start until 250°C, by means of isothermal time base thermogravimetric analysis, Maddalone[315] showed that while substantial volatilization of ammonium sulfate occurs at 205°C, the extent of volatilization is much smaller at 175°C. He further showed that sulfuric acid undergoes complete volatilization at 125°C and since it was logical to assume that at this temperature ammonium sulfate volatilization would be minimal, it could be possible to differentiate ammonium sulfate from sulfuric acid by microdiffusion at this temperature. In the final version of the method Maddalone, et al. chose to use

PDA-bromide as the immobilizing agent and microdiffused from polytetrafluoroethylene filters placed on a polytetrafluorethylene block at 125°C.[313]

The PDA-sulfate formed was then analyzed by a method developed by Maddalone, et al.,[313] through pyrolysis at 400°C in a nitrogen stream to yield sulfur dioxide, which was measured either by the West-Gaeke method or with a flame photometric detector.

Just prior to the publication of the PDA-sulfate diffusion-pyrolysis method, Leahy et al.[272] presented a thorough investigation of the possibilities of controlled volatilization. They achieved a ~ 90% separation between sulfuric acid, ammonium bisulfate and sodium bisulfate using volatilization temperatures of 190°C, 275°C, and 325°C, respectively. Ammonium sulfate was not investigated since it decomposes to the bisulfate at 250°C. The volatilization was carried out in quartz boats placed inside a heated quartz tube with a slow nitrogen purge. After each volatilization step the tube was removed, washed inside with water and the washings analyzed for sulfate turbidimetrically. Their attempts to apply the method to laboratory generated aerosol mixtures, was however, largely a failure. Very little sulfuric acid was recovered and results were erratic. They also found that even with polytetrafluoroethylene filters, sulfuric acid leaves a stain on the filter upon volatilization, indicating a reaction, which explained Maddalone's earlier observation[312] that there exists a definite cut off point of microdiffusion recovery at the lower end.

It is generally agreed now that thermal speciation of actual ambient air samples is unsatisfactory because of the enhanced reactivity of the free acid (which is reactive enough as it is) towards simultaneously collected particulate matter.[478] In a report awaiting publication[105] insitu volatilization has been accomplished for continuous monitoring, no differentation from ammonium bisulfate is of course possible.

Separation by Solvent Extraction:

Barton and McAdie[45,46] were the first ones to report a selective extraction of the free acid with isopropanol.

The extracted sulfuric acid was analyzed as sulfate by the chloranilate method. In later work,[47] the authors have reported automation of the system and minimization of interference due to other acids through pH control of the extract.

However, during the course of their radiochemical study, Maddalone, et al.[312] noted that isopropanol may not strictly be specific in extracting the free acid. This observation was later confirmed by the more detailed investigations of Leahy, et al.[272] who showed that although 2-propanol will not extract ammonium sulfate, it will quantitatively extract all the ammonium bisulfate and substantial amounts of any sodium bisulfate present. After examining a number of other solvents they recommended the use of benzaldehyde as the extracting solvent, since it was found to extract no detectible amounts of ammonium bisulfate, sodium bisulfate, ammonium sulfate and sodium sulfate.

In a later presentation, Tanner, Leahy and Newman[477] have

suggested a scheme of analysis: First an extraction with benzaldehyde to remove free sulfuric acid, then an extraction with 2-propanol to remove bisulfates, and then with water to remove soluble sulfates, each fraction to be analyzed by the flash volatilization - flame photometric detection technique.

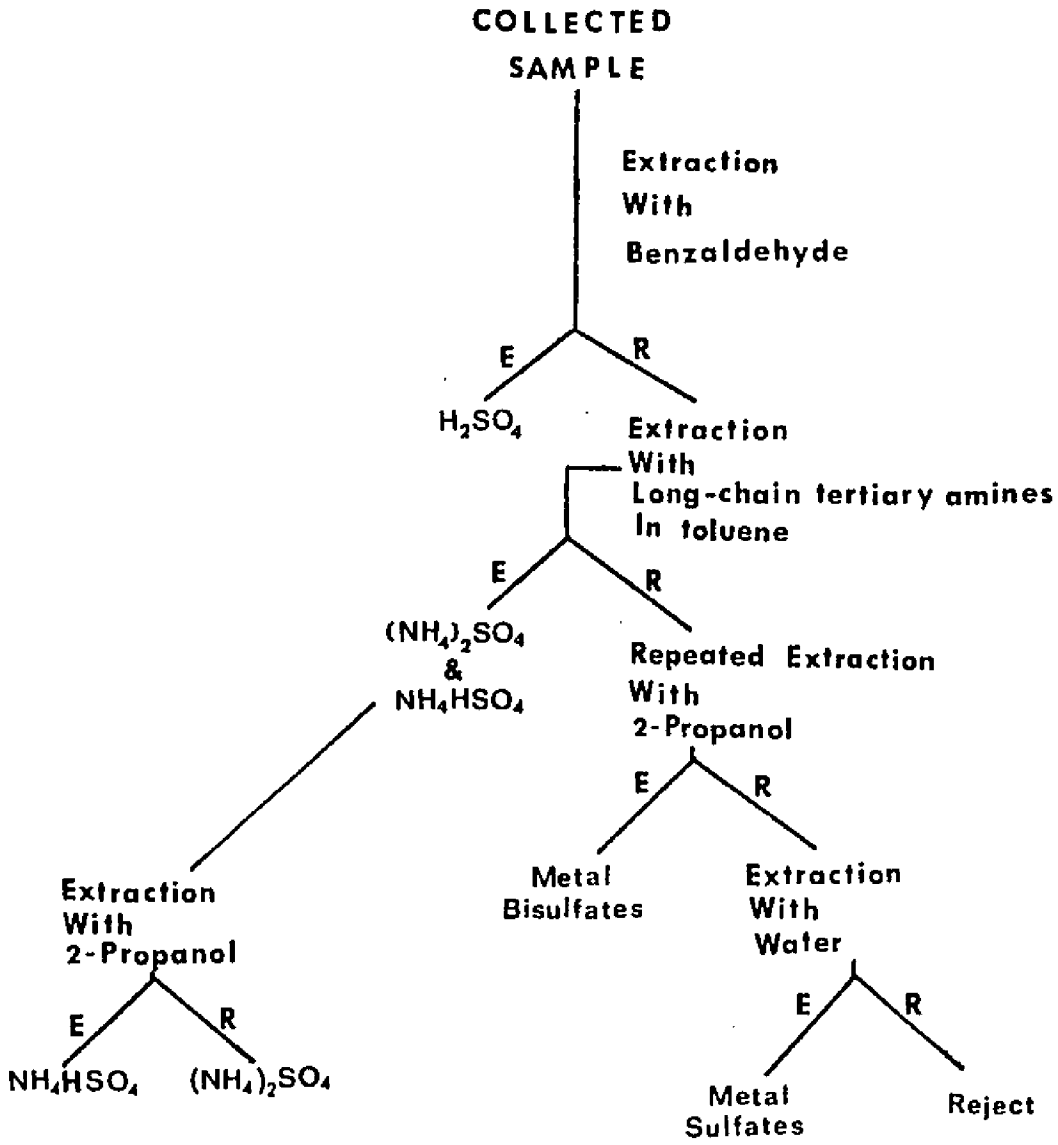
Stine[472a] has suggested an elaborate scheme based on the selective extraction of ammonium sulfate and possibly bisulfate from aqueous solutions into a solution of long chain tertiary amines in toluene, extrapolating from the reported behavior of ammonium phosphate.[332] Briefly the scheme is represented in Figure 2. Utility of this tediously long and untested procedure is questionable.

What all the proponents of solvent extraction apparently overlooked was the presence of other particulate inorganic salts such as chlorides or nitrates. It is logical to postulate that the presence of such salts and free sulfuric acid will lead to a metathesis in the presence of a solvent, liberating the corresponding acid and binding up the sulfate. A method that determines sulfate in the extractant and not acidity, may therefore, be subject to errors.

Separation Through Chemical Immobilization

As mentioned before, to obviate subsequent neutralization or other reactions it would be best if the acid aerosol could be immobilized or bound selectively at the moment of its collection. Thomas et al.[488] showed that when metal oxide particulates were collected on a filter after collection of about the same weight

FIGURE 2



E : Extracted Phase
R : Residue

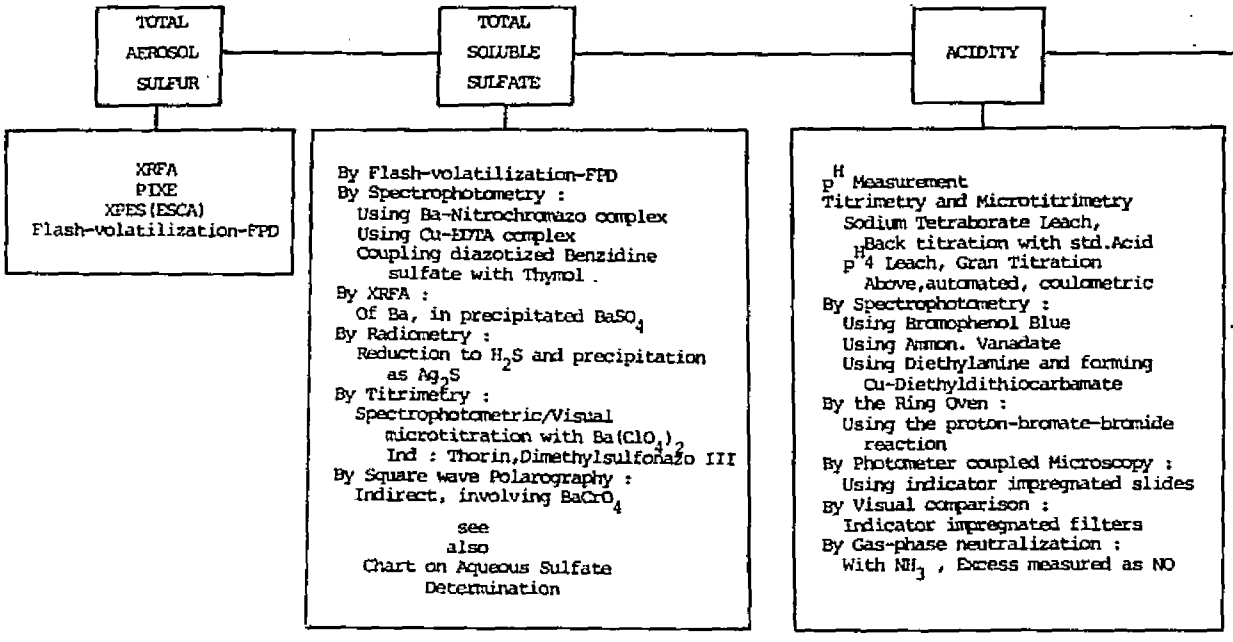
of sulfuric acid aerosol, no sulfuric acid could be detected by microdiffusion method.

The only method employing an impregnated filter reported so far is due to Thomas, et al., which immobilizes sulfuric acid aerosol selectively as opposed to any other acid aerosol (cf. Huygen[224]). The air was sampled through a glass fiber filter impregnated with solid PDA-bromide (the filter was soaked in 1.8% methanolic PDA-bromide solution and then dried at 80°C) and sulfuric acid which was present as a liquid aerosol, reacted with the reagent to form PDA-sulfate. The filter was subsequently pyrolyzed and PDA-sulfate decomposed to sulfur dioxide which was determined by a flame photometric detector or by the West-Gaeke method. While this filter gave the acid aerosol content, another identical filter was sampled simultaneously and then treated with a few drops of PDA-bromide solution before the pyrolysis step so that all the soluble sulfate was converted to PDA-sulfate. This yielded a value corresponding to the total sulfate content.[313]

While the method was sensitive, reproducible, rapid and capable of determining both the acid sulfate and total sulfate content, both ammonium sulfate and bisulfate interfered quantitatively in determining the aerosol sulfuric acid content. During pyrolysis, the ammonium sulfates apparentely decompose to sulfur trioxide which was reduced by the organic matter to sulfur dioxide. Further, it must be realized that the method essentially relied on sulfuric acid being a liquid aerosol, while the other sulfates exist as solid aerosols and therefore the difference in

topochemical reaction. Obviously, this assumption was invalid for high humidity sampling situations.

The present work towards the development of a method more specific to the sulfuric acid aerosol (which involves an identical sampling procedure save for one major modification) was conceived with the realization that immobilization at the moment of collection remains the best procedure to prevent the acid reacting subsequently with anything else. The problem then was to prevent interferences occurring from other sources, and to be able to differentiate the free acid from ammonium sulfate at all ambient humidity levels. A further desirable aspect was that it be a relatively fast and sensitive technique and that it should not involve very sophisticated instrumentation such that the technique could be quickly adapted to actual application.


TOTAL AEROSOL SULFUR
XRFA
PIXE
XPES(ESCA)
Flash-volatilization-FPD
TOTAL SOLUBLE SULFATE
By Flash-volatilization-FPD
By Spectrophotometry :
Using Ba-Nitrochromazo complex
Using Cu-EDTA complex
Coupling diazotized Benzidine sulfate with Thymol .
By XRFA :
Of Ba, in precipitated $BaSO_4$
By Radiometry :
Reduction to H_2S and precipitation as Ag_2S
By Titrimetry :
Spectrophotometric/Visual microtitration with $Ba(ClO_4)_2$
Ind : Thorin,Dimethylsulfonazo III
By Square wave Polarography :
Indirect, involving $BaCrO_4$
see also
Chart on Aqueous Sulfate Determination
ACIDITY
p^H Measurement
Titrimetry and Microtitrimetry
Sodium Tetraborate Leach, p^HBack titration with std.Acid
p^H4 Leach, Gran Titration
Above,automated, coulometric
By Spectrophotometry :
Using Bromophenol Blue
Using Ammon. Vanadate
Using Diethylamine and forming Cu-Diethyldithiocarbamate
By the Ring Oven :
Using the proton-bromate-bromide reaction
By Photometer coupled Microscopy :
Using indicator impregnated slides
By Visual comparison :
Indicator impregnated filters
By Gas-phase neutralization :
With NH_3 , Excess measured as NO

FLOWCHART 2

HALF A CENTURY AFTER AIRBORNE SULFATE (1921 - 1977)

ACIDITY

- p^H Measurement
- Titrimetry and Microtitrimetry
  - Sodium Tetraborate Leach, p^H Back titration with std.Acid
  - p^H 4 Leach, Gran Titration
  - Above,automated, coulometric
- By Spectrophotometry :
  - Using Bromophenol Blue
  - Using Ammon. Vanadate
  - Using Diethylamine and forming Cu-Diethyldithiocarbamate
- By the Ring Oven :
  - Using the proton-bromate-bromide reaction
- By Photometer coupled Microscopy :
  - Using indicator impregnated slides
- By Visual comparison :
  - Indicator impregnated filters
- By Gas-phase neutralization :
  - With NH_3 , Excess measured as NO

SPECIATING METHODS

DIRECT INSTRUMENTAL

- IR Spectroscopy,especially FTIR
- Optical and Electron Microscopy .
- on various substrates :
  - $BaCl_2$-Glycerol-Gelatin
  - $BaCl_2$-Glycerol-PVA
  - $BaCl_2$-Bromophenol Blue-Gelatin
  - Nitrocellulose-Methylenedisalicylic acid
  - Millipore filters, with later development
  - Ba-Rhodizonate on Millipore filters
  - Benzidine
  - Silver Nitrate
  - Graphite
  - Metal films : Fe,Cu
- Photometer coupled Microscopy :
  - On evaporated Iron films
- Spark Replica Counting :
  - Using acid-etched holes in a Polycarbonate filter
- Humidography : By change in light Scattering Coefficient with Changing Relative Humidity

INVOLVING PHYSICAL OR CHEMICAL SEPARATION

THERMAL SEPARATION

- By Microdiffusion :
  - At 195°C, on to NaOH
  - At 125°C, on to PDA-Br
- By Volatilization :
  - Successively at 190°C,275°C, 325°C on to a quartz tube
  - In situ, for continuous monitoring
- By Pyrolysis :
  - At 400°C, then reduction on Copper
  - Collection on Copper,direct pyrolys

SOLVENT EXTRACTION

- With 2-Propanol
- With Benzaldehyde
- Successively with 2-Propanol, Benzaldehyde,Water
- Untested Scheme : Involving Benzaldehyde, Long-chain tertiary Amines in toluene,2-Propanol,wat

CHEMICAL IMMOBILIZATION DURING COLLECTION

On Solid PDA-Br :

- Thermally reduce $(PDA)_2SO_4$ to SO_2 and measure SO_2
- Remove Xs reagent and measure $(PDA)_2SO_4$ Spectrophotometricall
- After nitration : This Work

A CENTURY
AFTER
RNE SULFATE
1 - 1977)

SPECIATING METHODS

POSSIBLE
FUTURE
METHODS

GC-FPD
GC-AA
RRS
LPIR
ILAMS
D^2-Spectrometry
Photoionization Mass Spec.
Plasma-source Emission Spec.

DIRECT INSTRUMENTAL

ctroscopy,especially FTIR
l and Electron Microscopy
ious substrates :
2-Glycerol-Gelatin
2-Glycerol-PVA
2-Bromophenol Blue-Gelatin
ocellulose-Methylenedisalicylic acid
ipore filters, with later development
hodizonate on Millipore filters
idine
er Nitrate
hite
l films : Fe,Cu
eter coupled Microscopy :
vaporated Iron films
Replica Counting :
g acid-etched holes in a
olycarbonate filter
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ttering Coefficient with
ging Relative Humidity

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At 125°C, on to PDA-Br
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on to a quartz tube
In situ, for continuous monitoring
By Pyrolysis :
At 400°C, then reduction on Copper
Collection on Copper,direct pyrolysis

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With 2-Propanol
With Benzaldehyde
Successively with 2-Propanol,
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Untested Scheme : Involving
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Amines in toluene,2-Propanol,water

CHEMICAL IMMOBILIZATION
DURING COLLECTION

On Solid PDA-Br :

Thermally reduce $(PDA)_2SO_4$
to SO_2 and measure SO_2

Remove Xs reagent and measure
$(PDA)_2SO_4$ Spectrophotometrically
After nitration : This Work

CHAPTER VI

BASIS FOR INTRODUCING CONTROL VALUES

"Elimination of CO, SO_x and direct particulates should alleviate problems associated with these primary contaminants. The term eliminate does not include methods which merely change the nature of the problem. Tall stacks reduce local SO_x ground level concentrations but also permit layering of high concentrations which can come to ground level at points many miles distant and fumigate plants and animals. Furthermore, the SO_x emitted aloft eventually ends up as H_2SO_4, which changes the acidity of rainfall, resulting in other detrimental effects on our environment.

Tall stacks only change the nature of the problem. At best they make the SO_x pollution more democratic and minimize health and odor complaints."

- E. A. Schuk, 1973

At the very outset of this Chapter it is perhaps wise to point out that it is impossible to write anything pertinent to allowable limits of air contaminants without provoking controversy. The intention of this author is not to recommend any particular values for allowable limits of either sulfur dioxide, sulfuric acid or suspended sulfates. Such an attempt would be quite beyond either the expertise or competence of the author. The purpose rather is to make an evaluation of the standards we have in force today, briefly look into the criteria they are based upon and comment on the bais upon which introduction of new standards should be made.

Introducing allowable limits of air contaminants poses such a controversial issue because two separate legal interests of our society are involved:

a) the right of each person to demand clean air and corresponding compensations for damages to health and property by foreign contaminants

b) the justifiable necessity for civilized survival in its present state, i.e., the requirements of heating, transportation and opportunities to earn a living in the industry.

At this point in human history, the two interests do not appear to be completely reconcilable. What we can hope for is the highest optimization of a tradeoff, economics vs. value judgments, both medical and ethical.

As Haagen-Smit[190] has stated, the medical expert might desire zero pollution but might ignore serious economic consequences of such policy.

With reference to our particular area of interest, Amdur's paper[17] on the toxicologic appraisal of particulate matter, oxides of sulfur and sulfuric acid should be regarded as essential reading for even remotely interested persons. She points out clearly that the standards for ambient and in-plant air quality cannot and should not be based on the same criteria. The population at risk is quite different in the case of community health effects as opposed to the average industrial worker, and as Amdur states so succinctly, "There is no reasonable need to control in-plant industrial atmosphere to the point where someone's 80-year old grandmother would flourish there."

Beyond a doubt one may choose to be somewhat extreme in interpreting such statements. In a discussion of Amdur's paper, Clayton[103] states: "If not overwhelmed by rapidity of change or too high concentrations of ambient contaminants man can probably meet the challenge of minimal airborne pollution. To what extent he protects the weaker members of his society is a value judgment." Indeed it is a value judgment, but what is the definition of minimal air pollution and who are the 'weaker' members of our society? Survival of the fittest may be valid for the animal kingdom but is it or should it be valid for homo-sapien-sapiens as well? The brewers of Westminster offered to burn wood instead of coal because the Queen of England was allergic to coal smoke but what are the chances that they would have made the same offer if it involved a hundred ordinary people? What is the extreme view in this regard? Back in 1958, Rush[426] wrote: "Man, a single species, has become an important geological and ecological influence on earth and his powers over the environment are increasing precipitately --- He threatens to sweep from the earth whole orders of life and in so doing he may

initiate irreversible changes that will sweep him off also."
We hope not.

Terminology of Standards and Some Prescribed Values

The West German authorities[278] have developed a rather succinct and thorough terminology for the control of air quality. They have chosen to define a new term 'immision' as the discharge of air contaminants permanently or temporarily near ground level, this being a part of the general emission picture. One would therefore refer to automotive exhaust as immissions and discharges from plant plumes in most cases as emissions. Because of the obvious consequence of discharge in or near the breathing zone, more stringent immision controls are necessary.

Haber's law[146] states that the deleterious effects of a specific substance is directly proportional to the total dosage, i.e., to the product of time of exposure and concentration. Unfortunately, this holds only for certain chemicals and short exposures at best. So definition of allowable standards in terms of measurement periods are necessary.

The VDI (Verein Deutscher Ingenieurs) defines

a) The MAK value as the maximum allowable concentration (8 hr. average, generally pertaining to industrial work sites), the synonymous term in this country is TLV (threshold limit value) administered by OSHA and is referred to as the MAC value in the United Kingdom and many other Countries. Unlike the MAK-values TLV and MAC values generally refer to 24 and not 8 hour exposures and are not to be exceeded more than once a year. Also, the term threshold limit value was originally introduced to indicate the threshold of perception, either by odor, irri-

tation or taste, etc., the term no longer bears the same connotation in general use.

b) The MEK value as the maximum allowable concentration of contaminant discharges at the source, or more importantly the total amount. EPA administers the prescription of such values in this country and is generally set on the basis of maximum permissible discharge amount per unit amount of product (energy, chemicals, etc.). They are referred to as source standards.

c) The MIK_K value as the maximum half hourly mean value that should not occur more than once in a given period. The MIK_K limit must be supplemented by its permissible frequency.

d) The MIK_D value as the sustained effect maximum value, i.e., highest permissible concentration at the ground level in ambient air (1/2 hour average) which may be allowed to be reached repeatedly but not exceeded.

Currently the MAK/TLV/MAC value for SO_2 is specified to be 13 mg/m^3 in most countries including the U.S. and Germany and 0.5 mg/m^3 in the U.S.S.R. MIK_K and MIK_D values for SO_2 in Germany have tentatively been held at 0.75 mg/m^3 (occurring not more than once in two hours) and 0.5 mg/m^3 respectively. In this country, the EPA has set some standards analogous to the MIK_K and MIK_D values, these are referred to as the primary and secondary standards for national ambient air quality.[235] The primary standard values for sulfur oxides are 80 $\mu g/m^3$ (annual average) and 365 $\mu g/m^3$ (daily average). The secondary standard values for the same are 60 $\mu g/m^3$ (annual average), 260 $\mu g/m^3$ (daily average) and 1300 $\mu g/m^3$ (three hourly average). The restrictions on the daily and 3-hourly values are that they

should not be exceeded more than once every year.

Athough standards for total airborne particulate matter in general has been set by the control authorities in various nations, no specific standards for sulfates has been set yet. It is evident from the discussions in Chapter III that there is an existent need to do so. As far as sulfuric acid aerosol is concerned, the only specified standard is the MAK/TLV/MAC value set at 0.3 mg/m^3 in the U.S.S.R. and 1 mg/m^3 in most other countries, including the U.S.

Some attempts have been made to specify the air quality by general indices, indices such as MAQI (Mitre air quality index), ORAQI (Oak Ridge Air Quality Index) and EVI (Extreme Value Index) have been defined aribitrarily on the basis of individual weighted root mean square sums (or a similar function) of individual contaminants such as CO, SO_x, NO_2, total particulates and total photochemical oxidants. For a detailed discussion of such parameters the interested reader is referred to the third annual report of the Council on Environmental Quality.[504]

ASSESSMENT OF AN AMBIENT AIR QUALITY STANDARD FOR SULFURIC ACID AEROSOL

The task of assessing an ambient air quality standard is ultimately with the epidemiologist. Epidemiologic studies however, have two major drawbacks: a) establishing a cause-effect relationship in an uncontrolled mobile population is a massive and time consuming undertaking and the degree of certaity attributed to any correlation depends largely on one's faith in statistics and the implicit assumption that there are no contributing parameters that have not been

taken into account. b) epidemiologic studies generally yield the needed information too late for the development of corrective measures. Amdur has commented that if she were to face the decision making problems of an epidemiologist, she would have long since joined the 'back to the kitchen movement' for women.

A decision for a standard then is not expected to be unequivocal, but there is the need for such a standard to be specified to prevent the misuse and misunderstanding of standards meant for other purposes.

One prime example of such misunderstanding is evident from a recent news item in Chemical and Engineering News.[99] The headline reads: "Catalytic converters are no problem" and goes on to state that based on a two-year EPA study in Los Angeles, sulfuric acid emissions due to cars equipped with catalytic converters did not lead to free acid aerosol levels that one needs to be concerned about, since it is substantially less than 1 mg/m^3.

Apart from the fact that it is very doubtful whether any reliable and dependable method was available at the time this study was started; 1 mg/m^3 is <u>not</u> the ambient air quality standard for sulfuric acid. This is the threshold limit value, meant for industrial atmospheres, and even as such is regarded by many as higher than it should be. (It is to be noted that this value is more than three times higher than the corresponding Russian standard.) The news item did not state what the measured levels actually were nor what the particle size distribution was. The suggestion that scientists were afraid that amibient air

concentrations of sulfuric acid might be near the TLV due to catalyst equipped automobile emissions is preposterous; in fact, the maximum likely roadside concentrations estimated before the beginning of the study was 150 $\mu g/m^3$.[450]

EPA's own authorities estimated that acute asthmatics constitute some 2 - 5% of the total population and there are four times as many people with chronic respiratory diseases. With this in mind and considering that in her work Amdur[13] originally suggested a value of 0.25 mg/m^3 as a tentative ambient air standard for sulfuric acid, there seems to be little justification to be excited about the fact that ambient air has not reached the threshold limit yet. Further, since Amdur's original study, more recent work has led investigators[4] to suggest that this value (0.25 mg/m^3) does not leave an adequate safety margin. As has been mentioned in Chapter III the recent study of Alarie[5] shows definite histopathological changes in the lungs of experimental animals even at 100 $\mu g/m^3$ as a result of long term exposure.

One of the characteristics of acquisition of knowledge is that our areas of ignorance become better defined and more acute. It is known now that the hazards posed by aerosol sulfates are very largely size dependent but it has still not been unequivocally established in what particle size fraction free sulfuric acid is dominantly present. It is more than probable that the acid aerosol resulting from automotive emission is concentrated in a much smaller size fraction than sulfuric acid resulting from the oxidation of sulfur dioxide in the ambient atmosphere.

It is also quite certain that in the future, air quality standards will be based not only upon concentration but also the particle size of the species concerned.

At the present moment an ambient air quality standard specification of aerosol sulfuric acid is sorely needed and enough toxicological data is available for establishing a tentative value. Without specified control values, matters have a nature to go from bad to worse. A few years ago when a subway strike caused drastically increased automobile use in Paris, nearly a thousand tons of sulfuric acid was reported to be present in the total air mass of the city. Electricité de France had to install a monstrous ambient air filtering system (essentially an oversize vaccuum cleaner with a series of filters, processing about 16000 m^3/day) in a particularly congested location.[357] With properly established and enforced standards such desperate measures can hopefully be avoided.

A GLIMPSE INTO THE FUTURE: A CRITICAL OUTLOOK FOR CONTROL

It must be realized first of all that the problem of sulfur oxide contamination is to be dealt with on a local rather than a global basis. Even if the release of sulfur dioxide into the atmosphere through human activities were totally stopped, the natural emission of hydrogen sulfide would continue and the concentration of sulfate aerosols in the stratosphere will not be significantly altered. As a matter of record, the levels of sulfate aerosol in certain stratospheric layers are four times greater than background concentrations at the ground level.

Direct emission of sulfuric acid from automotive exhausts can and should be stopped. Better catalysts are becoming available for this purpose and with the advent of selective oxidation mixed bed catalysts,[302,459] there will be no need to make a tradeoff. This of course does not solve the more general problem. The problem is not so much the emission of sulfur dioxide per se, but its conversion to sulfuric acid and sulfates which are far more hazardous than the parent contaminant. Unfortunately, industry supports the growth of industry around it and the contamination of ambient air is rarely due to one major species. Wherever the sulfur dioxide concentration is high, amounts of catalytic agents and photooxidants released into the atmosphere are also high and the conversion rate to sulfates is high. It is possible that just by measuring sulfur dioxide, sulfuric acid, and sulfate aerosol concentrations, a very good estimate can be made as to the extent other contaminants are present and the air quality assessed. Under any circumstances, it is obvious that as far as sulfur contaminants are concerned, sulfur dioxide data by itself cannot be regarded as a valid measure of air quality without the attendant measurement of its ocidation products. Chambers[92] said succinctly: "... the full air pollution potential of SO_2 is realized only after it has reacted with other substances in the atmosphere."

When we quote figures of sulfur dioxide emission in millions of Mtons, the magnitude is often incomprehensible. When the data are broken down on emission/person/year basis, the amounts become

almost staggering. Smith and Jeffrey[461] reports that in the United Kingdom about 100 Kg of sulfur dioxide is emitted per year per person. They have also shown that the emission from any given town can be estimated quite accurately on the basis of a value of 50 Kg/member of the population multiplied by an industrial factor. From non-industrial residential areas to heavily industrialized cities this factor varies from 0.5 to 2.0. In this country, the emission figures per person are even higher, no doubt due to a more energy extensive economy. In Table I on the next page the amounts of sulfur oxides emitted per person per year has been calculated from the available census data[497] and the estimated sulfur oxide emissions.[91]

The percentage contribution of fuel combustion in stationary sources to the total sulfur oxide emission was calculated from the emission data. The figures show that this has remained the major and virtually constant contributor to the total amount emitted. In 1960 the celebrated photochemist Leighton[277] wrote: "In a sense our pollution may be likened to a weed. Controls may clip back the weed, but will not keep it from growing again. To kill the weed we must get at the root, and the root of the whole problem of general pollution is combustion ... The proper approach to a lasting solution of these problems, the only way to kill the weed, is to attack, not the product of combustion, but combustion itself, to reduce by every possible means the burning of fuels in favor of non-polluting sources of heat and power."

Heat and Power. Our Energy Needs. It is always easy to blame

TABLE I

SULFUR OXIDE EMISSION THROUGH THE YEARS

	YEAR					
	1940	1950	1960	1968	1969	1970
U.S. Population (millions)	132	152	181	201.	203	205
Total SO_x emission (millions M tons/yr.)	21.5	23.8	23.3	31.3	32.4	33.9
SO_x Emission per capita (Kg/yr.)	163	157	129	155	159	165
SO_x emission from stationary sources (Per cent of total)	78.1	77.3	75.1	79.2	77.0	78.2
SO_x emission from steam electric power plants (Per cent of total)	13.0	22.7	43.3	55.6	56.5	57.2

the industry for pollution, because industry represents a faceless body that can easily be accused. A look at Table I reveals that during the course of the past thirty years the contribution of sulfur oxide emissions due to steam - electric power plants have been steadily escalating. It is useless to blame the industry per se. The industrial output is eventually consumed by the public, which in turn is responsible for its individual lifestyles. The key factor is energy consumption. In this country, in the immediately foreseeable future, more and more lower grade coal would be burned to meet energy needs. Without a massive and extensive undertaking to desulfurize such fuel, both sulfur dioxide and its attendant contaminant concentrations will go up. An excerpt from the noted ecologist Odum[368] is quoted as the concluding paragraph.

"Only a small part of the total controlled energy is now processed by the individual person or by work that is recognizably personal. More and more energy flows are in the machines of the system.

We may wonder whether the individual human being understands the real source of the bounty to him of the new energy support. How many persons know that the prosperity of some modern cultures stems from the great flux of oil fuel energies pouring through machinery and not from some necessary and virtuous properties of human dedication and political designs? It is not easy to fit into our thinking the concept that part of the energy for growing potatoes came from fossil fuel. In the new system much of the higher agricultural yields are only feasible because fossil fuels

are put back into the farms through the use of industrial equipment, industrially manufactured chemicals and plant varieties kept in adaptation by armies of agricultural specialists supported on the fossil fuel-based economy."

PART II

EXPERIMENTAL

"One must learn by doing the thing; for though you think you know it, you have no certainty until you try."

- Sophocles

CHAPTER VII

DEVELOPMENT OF METHODOLOGY

PRELIMINARY RESULTS

EQUIPMENT AND REAGENTS

DEVELOPMENT OF METHODOLOGY - PRELIMINARY RESULTS

The primary objective of this research program was to develop a relatively fast and precise method to determine aerosol sulfuric acid in the ambient air and to differentiate it from ammonium sulfate if possible. Two points were perceived at the outset:

a) The method must have high sensitivity, because large sampling volumes not only are time consuming but might actually yield erroneous results (cf. Chapter V)

b) Immobilization at the moment of collection remains the best way to prevent the sulfuric acid from reacting with any other material collected simultaneously and PDA-bromide is the best available reagent for such immobilization.

The original idea was to find a dye that might be selectively adsorbed by PDA-sulfate and not by PDA-bromide with which the sampling filter was impregnated. Sampling would be done by using a dye + PDA-bromide impregnated filter and often sampling excess reagent and unadsorbed dye would be washed or eluted off, possibly on the ring oven. The adsorbed dye would then be liberated by some drastic treatment (e.g. with concentrated hydrochloric acid) and the dye eluted to the ring zone would give a measure of the amount of PDA-sulfate present and thence the sulfate. A number of dyes belonging to the structural class of methyl orange were found to fit these requirements but it was discovered that every one of these dyes also has a strong affinity for metal oxide particulates as well as for carbonaceous material, e.g., soot. Therefore, this course was no longer pursued.

A slightly modified approach involved the investigation of dyes that may have altered chemical reactivities after chemisorption (or occlusion in the crystal* during the formation of the PDA-sulfate) such that it may be differentiated from the free or physically adsorbed dye.

Fuchsin and eosin were investigated. Sulfite bleaching of fuchsin occurred just as easily with the dye adsorbed onto PDA-sulfate as with the free dye, indicating no chemisorption occurred. The bromination reaction of eosin to produce fluorescein was utilized in the second case, and in this case something unexpected occurred. With the dye in the presence of PDA-sulfate, the material turned dark brown upon the addition of bromine water. It was soon revealed that this intensely brown material was being produced from the reaction of bromine-water and the PDA-sulfate itself, in fact a similar reaction took place with PDA-bromide and bromine water, indicating the reaction to be characteristic of the organic cation and not of any particular salt.

It was thought at first that the reaction was essentially an oxidation and similar reactions were attempted with chlorine water, iodine vapor, acidic hydrogen peroxide and concentrated nitric acid.

All of these reactions were carried out in trace quantities on filter paper as a medium. Chlorine water produced a greenish yellow coloration. Iodine vapor yielded a brown material reminiscent

---

*An example of this type of behavior is that of oxalic acid reduction immune permanganate, when the latter is occluded in the barium sulfate crystal lattice.[150]

of the product formed with bromine water but was somewhat less intense in color. No reaction was observed with acidic hydrogen peroxide (alkaline reagents rapidly attacked PDA-salts, the free amine was liberated and that was rapidly oxidized by air to greenish black tarry products) and nitric acid produced a very intense yellowish green product.

Except in the case of the nitric acid reaction the products were very insoluble and could not easily be eluted from the spot at which they were formed. The nitric acid product eluted quite easily with a number of solvents (acetone, methanol, etc.) and it was not known at the time whether the excess free acid present played any role in such solubiilities.

It was realized that although the reaction with nitric acid was not uniquely characteristic of the sulfate salt of PDA (the impregnating reagent PDA-bromide or any other PDA salt would yield the same product), this might still be utilized as the basis of a measurement method by virtue of the fact that PDA-sulfate has very distinctive solubility characteristics.

PDA-sulfate is very insoluble while PDA-Br is quite soluble and therefore the latter may be removed by washing or elution.

Thus, after removal of the impregnating reagent the PDA-sulfate on the filter may be treated with nitric acid and, provided the reaction is reproducible, measurement of the developed color intensity either through spectrophotometric or ring oven techniques would yield the amount of PDA still remaining and thus the amount of sulfate.

The reaction proved to be reproducible but removing the large excess of PDA-bromide leaving the very small amount of PDA-sulfate formed during sampling turned out to be much more difficult than was originally envisioned. Various washing solutions and washing techniques were investigated. The original work was done with impregnated glass fiber filters which were prepared according to the procedure described by Thomas, et al.[488] A 102 mm diameter Gelman Spectrograde-A filter was cut so that it just fitted inside a 100 mm. diameter petri dish. A solution of 180 mg PDA-bromide in 10 ml methanol was poured over the filter. After five minutes the filter and the dish were placed inside an oven at 80°C to evaporate the solvent. Once the solvent had evaporated the filter was cut into 16 mm discs by means of a filter cutter. These discs were placed on a support with an annular opening slightly smaller than the filter so that the bottom of the filter was not in contact with any solid surface.

The center of the filter was then moistened with two drops of 95% ethanol followed by an aliquot of sulfate solution. Without alcohol premoistening, aqueous solutions tended to 'bead' on the filter and did not penetrate.

The excess reagent was washed off with a solvent under investigation using various techniques. The filter was then placed in a small funnel which in turn was placed in a 10 ml. volumetric flask. The solvent was allowed to evaporate, the filter remoistened with acetone, and then washed with 4 ml. of concentrated nitric acid. The color development reaction was almost instantaneous.

The volume was made up to the mark with water and the absorbance was measured in a 1 cm cell at 420 nm, which preliminary investigations showed to be the absorption maximum in the visible region under such conditions.

Various washing techniques were attempted using 25 ml of 95% ethanol as wash solvent. After placing the filter on a sintered glass support washing was done manually with a disposable pipet, with a buret, a buret fitted with a capillary tip, and a constant head buret. The total washing time in case of the burets was maintained constant at 5 minutes. Analytical results at levels of sulfate below 5 μg were erratic in all cases and showed poor precision. Seemingly the erratic results were due to the physical removal of the poorly retained precipitate on the filter rather than its actual dissolution.

A different washing technique was found to give acceptable results yielding standard deviations of 10% or better, down to the 1 μg range. This involved heating ca. 150 ml. of wash solvent to boiling, and pouring ~ 25 ml. of it on filters (generally a batch of five or six) kept in a 50 ml. beaker, allowed to equilibrate for a minute and then decanting off. Then the filters were treated with another ~ 25 ml. of hot solvent, the process being repeated four times. This technique was explored thoroughly and the finally adapted version utilized a one-minute wash for the first wash and thirty second intervals for the four subsequent washes. This method was superior to the other techniques attempted not only in terms of better precision (standard deviation of 5% or

better at sulfate levels between 5 and 50 μg and between 5 and 10% between 0.5 and 5 μg) but also in terms of analysis time, since a number of filters could be washed at the same time.

Later it was realized that by the very simple expedient of using a filter strip (only a part of which was impregnated) the excess reagent could be removed very easily by frontal chromatography. This constituted the basis of the final analytical technique and will be described in detail in the following chapter.

With the possibility of aqueous sulfate determination in mind, interference by other anions was investigated using the hot ethanol wash technique. Both phosphate and oxalate were found to interfere substantially and it was thought that a more acidic wash solvent may be able to reduce the interference.

The following wash solutions were investigated, the solvent in each case being 95% ethanol: 4N HCl, 2N HCl, 0.5 N HCl, 0.03N HCl, 0.03N HCl saturated with NaCl, 0.03N HCl saturated with NH_4Cl, 0.25N HCl + 0.5N Potassium hydrogen phthalate, 0.25N HCl + 0.5N sodium citrate, 0.25N HCl + 0.25N borax, saturated NH_4Cl, 1% trichloracetic acid, 10% monochloroacetic acid, 5% monochloroacetic acid, 1% monochloroacetic acid and 0.5% monochloroacetic acid.

Phosphate was chosen to be the representative interfering ion. The study showed that systems containing free hydrochloric acid remove not only phosphate but also part of the sulfate and was generally unacceptable due to much poorer sensitivities. The phthalic, citric and boric acid systems did not work either, these ions themselves began to interfere at the high concentrations

involved. Ammonium chloride solutions showed no perceptible difference from alcohol by itself, and trichloroacetic acid proved to be just as unacceptable as hydrochloric acid. A one per cent solution of monochloroacetic acid was chosen as the best compromise to be used only for extreme cases where large amounts of interfering ions might be present. With the washing technique used at that time, this solution did wash off a small but perceivable amount of sulfate. The calibration curve was close to that obtained with the 95% ethanol wash but was not identical.

Possibly the most difficult task encountered during the entire course of this work was to establish the identity of the product formed. One erroneous assumption led to another and a number of new compounds were isolated and characterized and they served to show where the mistakes in original assumptions lay. The compound of interest was the very last one to be characterized, proving, perhaps, the infallibility of Murphy's laws. The effort, however, was not spent in vain, since the chemistry of the compounds isolated turned out to be very interesting and therefore rewarding.

Initial studies showed that the reaction product of PDA-sulfate with concentrated nitric acid under the conditions used in the determinative procedure (tobe described in the next chapter) behaved as an indicator. The absorption maximum of this compound is strongly acidic solutions was centered around 420 nm and that in strongly basic solutions was centered around 550 nm. Structural studies (to be described in Chapter XI) proved this compound to be

2-amino-4,6,9-trinitroperimidine* and the absorbance vs. concentration behavior of the compound was studied in 3N nitric acid and 1N sodium hydroxide at 420 nm and 550 nm respectively. The plot is shown on Figure 3 and it is apparent that the compound conforms to Beer's Law within the range studied (up to ~ 10 μM concentration).

EQUIPMENT, REAGENTS AND GENERAL AUXILLIARY PROCEDURES

REAGENTS: All chemicals used in this study were of analytical reagent grade, unless otherwise stated.

Perimidinyl ammonium bromide (PDA-bromide): Stephen[469] introduced the PDA cation as a sulfate precipitant and synthesized the chloride salt according to the method of Sachs.[430] The method was cumbersome and McClure[305] developed a much simpler synthetic route to prepare the bromide salt. The product still needed many recrystallizations before it could be used. During the course of this work substantial modification of McClure's original method was made leading to a purer product in higher yield. A copy of the paper by Dasgupta, et al. is given in Appendix I. A 1% w/v solution of the reagent in methanol was used by dissolving 100 mg. of anhydrous PDA-bromide in 10 ml. of methanol. Slight warming is necessary to effect dissolution. Both the solid and the solution were stored in dark bottles because the reagent apparently undergoes photodecomposition. By itself, the solution begins to deteoriate after a month. Addition of 10 mg of

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*This compound is referred to as amino nitroperimidine in the following two chapters, in an effort to save space.

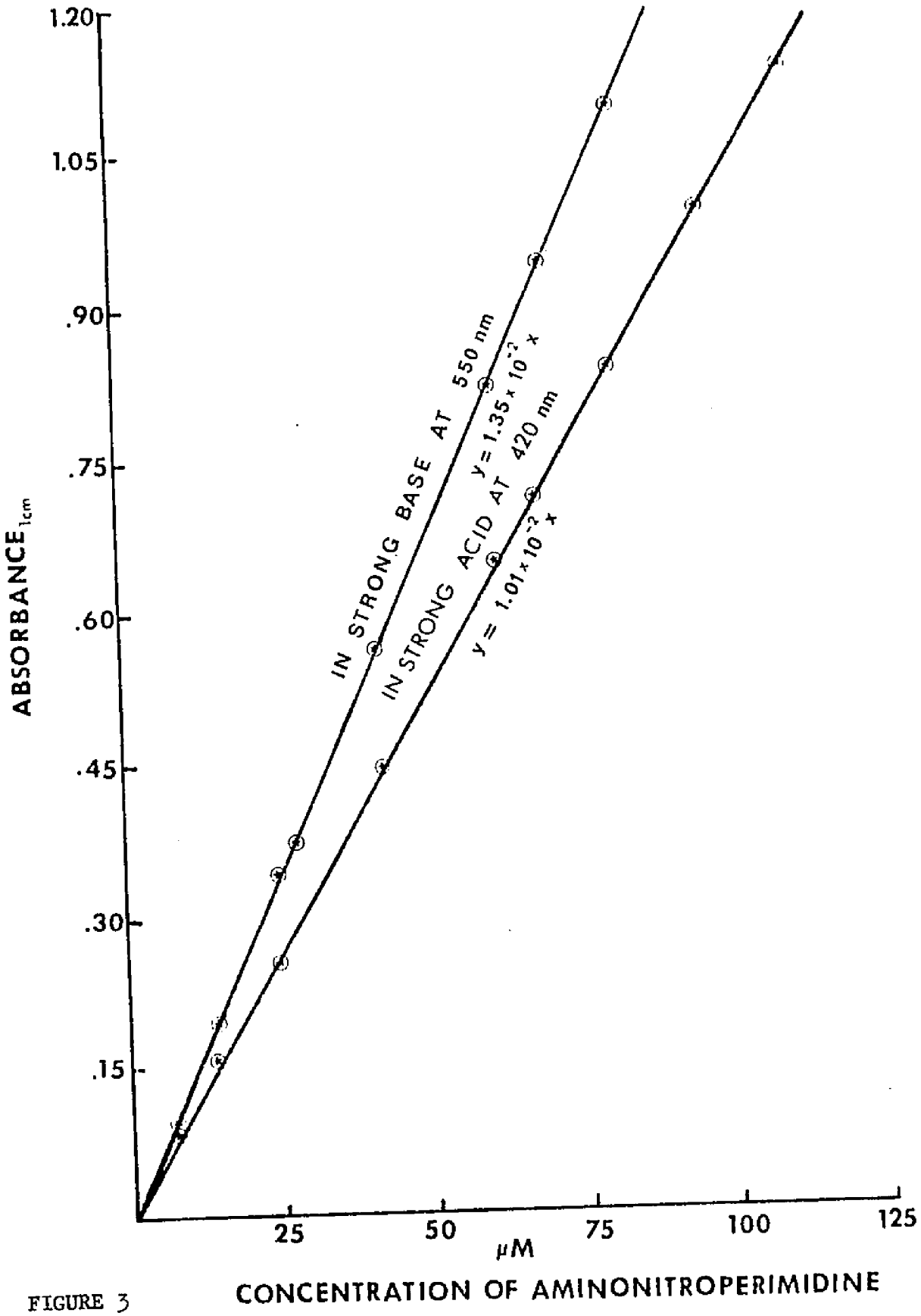

1.20
1.05
.90
.75
.60
.45
.30
.15
ABSORBANCE 1cm
IN STRONG BASE AT 550 nm
y = 1.35 x 10^-2 x
IN STRONG ACID AT 420 nm
y = 1.01 x 10^-2 x
25
50
75
100
125
μM
CONCENTRATION OF AMINONITROPERIMIDINE

FIGURE 3

t-butyl hydroxy toluene (BHT) per 100 ml of solution improves shelf life to six months, and was not found to affect any results. However, since very little reagent is used at a time in these microanalytical techniques, making a larger stock with a longer shelf life is merely a matter of choice.

Sulfate standard solutions: 1.814 g potassium sulfate was dissolved in 100 ml of solution to make a 10,000 ppm (10 $\mu g/\mu l$) sulfate stock solution. This solution was sequentially diluted with distilled deionized water to prepare more dilute standard sulfate solutions and stored in polyethylene bottles.

A 100 ppm sulfuric acid solution and a 200 ppm ammonium sulfate solution was used for the generation of the acid aerosol and the ammonium sulfate aerosol respectively; the concentration of neither was critical.

Anion solutions: 10,000 ppm stock solutions were prepared for each anion tested in the interference study of aqueous determinations. Sodium or potassium salts of the following anions were used: chloride, fluoride, bicarbonate, nitrate, hydrogen phosphate, acetate, formate and oxalate. The solutions were stored in polyethylene bottles and diluted as needed.

Sodium hydroxide (4N): 160g of sodium hydroxide was dissolved in a liter of solution. Concentration was not critical.

Monochloroacetic acid: A 1% solution in methanol was made by dissolving 10.00 g of the acid in 1 liter of solution. This reagent will be referred to as MCAA in the rest of the text.

Barium acetate solution: A saturated solution of barium acetate

in 25% methanol and 75% acetone (by volume) was used.

Other reagents used will be mentioned concurrently with the description.

EQUIPMENT AND GENERAL PROCEDURES:

Spectrometry: A Beckman DB uv-visible spectrophotometer was used along with a 1 cm glass cell for direct absorbance readout of all quantitative measurements.

A Beckman DB-G uv-visible spectrometer in conjunction with either a Beckman recorder or a Sargent SR-G recorder was used for spectral studies. In later stages of the work when pH dependent absorption spectral studies were undertaken, data reduction from recorder plots proved to be a gargantuan task and the Beckman DB was interfaced with a Data General NOVA 1200 computer system equipped with a teletype and paper tape puncher. The Beckman DB could not be interfaced directly to the computer, an interfacing device was specifically designed for this purpose. The schematic and functional details of this interfacing device is given in Appendix II. The data on paper tape was transferred to a Diskette and processed subsequently at the LSU/SNCC IBM 360 computer system facilities. Initial plots were made using the Varian Electrostatic plotter and final versions were plotted in the Versatek pen and ink plotter located in the Coastal Studies Institute.

A Perkin Elmer 137 sodium chloride spectrophotometer was used for quick infrared scans and high resolution scans were made with the Perkin Elmer 621 grating spectrophotometer. All

spectra were run in KBr pellet form, using spectrograde KBr, Crescent 'wig-L-Bug' dental filling mixer, a Perkin Elmer pellet dye and a Wabash-Hein-Warner hydraulic laboratory press.

Preliminary nuclear magnetic resonance spectra was taken with the Varian A60A NMR spectrometer, and 100 MHz NMR spectra were run by Mr. John Martin on the Varian HA-100 spectrometer. The very small availability of certain samples necessitated the use of Fourier Transform spectrometry and FT-PMR spectra as well as ^{13}CMR spectra were kindly provided by Dr. H. Frances Walker-Merrick of Dow Chemical Co., run on the JEOL-FX-60 spectrometer at their Freeport, Texas facilities.

The mass spectral analysis of compounds of interest could not be done at the facilities available at LSU because of lack of both resolution and accuracy. Mass spectra were provided by the courtesy of Dr. P. K. Das of the University of Houston, run on their Hewlett-Packard 5360A GC-MS System. In addition, some preliminary mass spectral scans were kindly provided by Dr. D. K. Wolcott of Dow Chemical Company, Plaquemine, Louisiana. Other Analyses: Polarographic studies at the dropping mercury electrode (DME) were conducted with a Sargent model XV recording polarograph in conjunction with a Sargent model-A IR compensator. Thermal studies were carried out with a Dupont 900 thermal analyzing system in conjunction with the Dupont 950 thermogravimetric analyzer.

Preliminary elemental analyses were carried out by Mr. R. L. Seab, supplemented later with analyses made by Galbraith

Laboratories of Knoxville, Tennessee; who also provided molecular weight data based on osmometric measurements.

Microphotographs were taken on a Leitz Ortholux II research microscope equipped with a Leica-Orthomat photographic system located in the Plant Pathology Department.

Sulfuric acid aerosol was generated by using the generator described by Thomas, Dharmarajan and West.[486] Essentially the apparatus consists of an atomizer burner mounted at the bottom of a Pyrex tube, 150 cm in height and 9.5 cm in diameter. The burner is operated with acetylene-oxygen mixture and a dilute sulfuric acid solution was concurrently aspirated into the flame. Sulfur trioxide was generated which reacted with the water vapor present to form sulfuric acid aerosol with particles between 0.1 - 5 μ in MMD. The sampling probe is inserted through the top center of the stack to a depth of about 120 cm from the burner tip. The sampling was accomplished by drawing air through the sampling probe by a slightly modified Gelman 23000-1 filter tape sampler. The generator was operated at least five minutes before sampling, such that equilibrium was attained in the stack.

A Macrosonics 125 VF ultrasonic generator was used to generate ammonium sulfate aerosol. Sampling was accomplished by the same Gelman tape sampler mentioned above.

To produce humidity controlled aerosol streams, the directly generated aerosol samples were diluted with dry nitrogen from a compressed gas tank. Humidity was measured with a Lab-line 2200 electrohygrometer. Flows were controlled with needle valves

in conjunction with appropriate range flowmeters, supplied by Fisher and Lab-crest. The flowmeters were accurate to ± 2% of full scale.

Results obtained by the method developed in this study was cross checked by comparison with data obtained on identical samples by the method developed by Thomas, et al.[488] Essentially, the comparison method was based on: a) formation of PDA-sulfate on a PDA-bromide impregnated filter by topochemical reaction with the acid aerosol, b) subsequent pyrolysis of the filter leading to the decomposition of PDA-sulfate yielding sulfur dioxide, c) measurement of the evolved sulfur dioxide by either the West-Gaeke method[166] or a flame-photometric sulfur monitor. The pyrolysis furnace and the combustion train has been described by Maddalone, et al.[313] For this study, a Bendix 8300 flame photometric total sulfur monitor was used in conjunction with a miniservo recorder to measure the sulfur dioxide. Although this method was not as precise as the West-Gaeke method, it was substantially faster.

MISCELLANEOUS:

Various sundry laboratory equipment such as hot plates, magnetic stirrers, ultrasonic baths, (Fischer model CT with cleaner model SS-O) etc. were utilized during the course of this study. The Thomas Trace Oven was used for ring oven studies. All glassware was cleaned by overnight immersion in chromic acid, followed by washing first with water, then with soap solution and finally washed repeatedly with distilled deionized water.

Volumetric glassware used conformed to NBS grade A standards. Microliter pipets used for aqueous sulfate determinations ranged from 1 - 100 λ (microliters) in volume (E. H. Sargent and Co., Accuracy $\pm$ 1%). Automatic pipets (A. H. Thomas and Co.) of 1 ml. capacity were used for quick addition of sodium hydroxide solutions and acetone involved in the determination procedure, the exact amount of these reagents not being critical.

CHAPTER VIII

THE DETERMINATION OF AQUEOUS SULFATE

I. CALIBRATION WITH AQUEOUS SULFATE:

102 mm diameter ultrapure Glass Fiber filters (Gelman Spectrograde A) were cut into 18 x 72 mm strips. These filters were alwyas handled with Teflon tipped stainless steel forceps. A filter strip was laid down on a Teflon ring with a $\sim$ 15 mm diameter annular opening and so placed that the bottom of the strip was about 20 mm from the center of the aperture. A guide mark was inscribed on the Teflon ring to facillitate positioning. The strip was then covered with another identical ring, to keep it in place. One drop of 1% methanolic PDA-bromide was next added from a disposable pipet to the strip at the center of the aperture followed by an aliquot of standard sulfate solution from a microliter pipet. In practise the microliter pipet was filled up to the mark and made ready first so that the transfer can be made as quickly as possible and the loss of methanol by evaporation thus minimized. The microliter pipet tip was touched lightly against the filter surface and held at an angle approximately 15^{o} from vertical to facilitate rapid transfer. When the transfer was complete, another drop of PDA-bromide was added to the same spot and the strip removed and dried for three minutes in a stream of filtered cold air from a small portable hair dryer.

Methanol was poured in a 250 ml tall form Griffin beaker to a depth not exceeding 5 mm. The filter strips were lowered into the solvent one at a time. Five strips could be treated simultaneously at one time and so all determinations were carried

out in sets of five. The strips were allowed to remain in the beaker for a period of at least ten minutes and not exceeding fifteen, during which time methanol moved up and carried the unreacted PDA-bromide with it. The strips were placed one at a time on the Teflon rings positioned as before and the area surrounding the injection spot was cut away with a 25 mm diameter stainless steel filter cutter. The strip width was smaller than the diameter of the filter cutter and therefore the cut piece had the appearance of a square with two crescent edges. The pieces were placed inside 32 mm diameter glass funnels which in turn were resting on 10 ml. volumetric flasks held in a stand.

Calibration curves were constructed for both measurement in acidic solution and basic solutions and the treatment was different in each case.

a) Procedure for measurement at 420 nm in acidic solutions

Methanol was allowed to evaporate from the filter until the filter was moist but no longer thoroughly wet. Six drops of concentrated nitric acid was added from a disposable pipet to the filter, distributing as evenly as possible. The material on the filter was then allowed to react for a minute and then washed down with 2 ml concentrated nitric acid from an automatic pipet, 1 ml at a time and slowly, patting, and pressing the filter against the funnel surface with the pipet tip to facillitate the removal of all of the colored material formed. The solution was then made up to the mark with water, mixed thoroughly and poured into 1 cm glass cuvettes through a funnel which had its stem

lightly packed with good quality glass wool to remove the pieces of glass fiber that unavoidably came from the glass fiber filter. Absorbance at 420 nm was then measured and recorded.

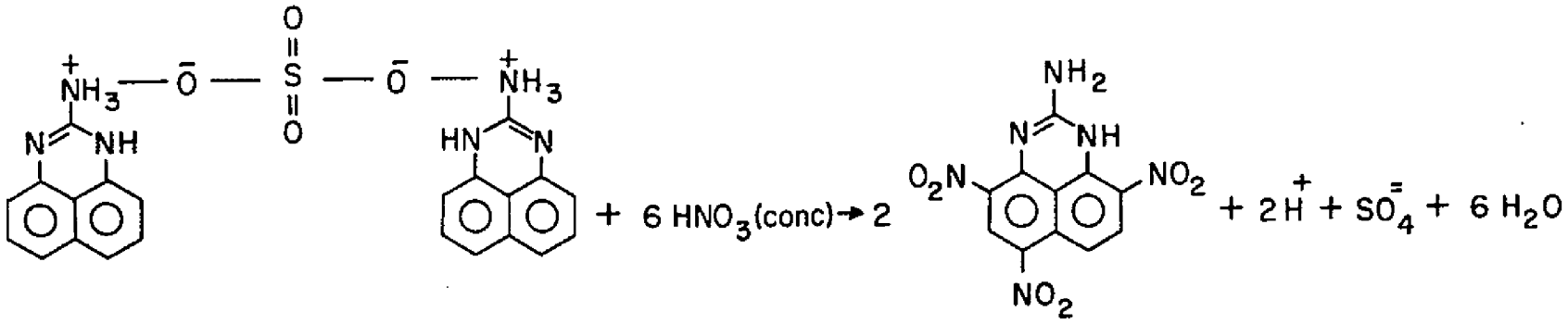
b) Procedure for measurement at 550 nm in basic solutions

As before the filter was allowed to react with six drops of concentrated nitric acid for a minute and then the colored product formed was washed down with 1 ml of acetone from an automatic pipet, patting and pressing the filter against the funnel surface to facillitate removal of the colored product. Two milliliters of 4N sodium hydroxide were added next, again using an automatic pipet and the solution made up to the mark with water. The solution was thoroughly mixed and filtered into the measuring cuvette as before, and absorbance was then measured at 550 nm.

II. RESULTS:

Sulfate ion was liberated and 2-amino, 4,6,9-trinitroperimidine was formed when nitric acid reacted with PDA-sulfate on the filter under the conditions described (Figure 4). Calibration curves in acidic and basic solutions are given in Figures 5 and 6 respectively. The data are plotted in terms of the parts per million sulfate ion concentration in the measuring volume. The total volume in this case was 10 ml and therefore without the multiplication factor of 10^{-1}, the plot can be read directly in terms of micrograms of sulfate put on the filter. It was apparent from the plots that the calibration curve was linear within the range studied (up to 50 μg of sulfate; although the plot shown for basic solutions does not go up this high, it was linear up to

FIGURE 4



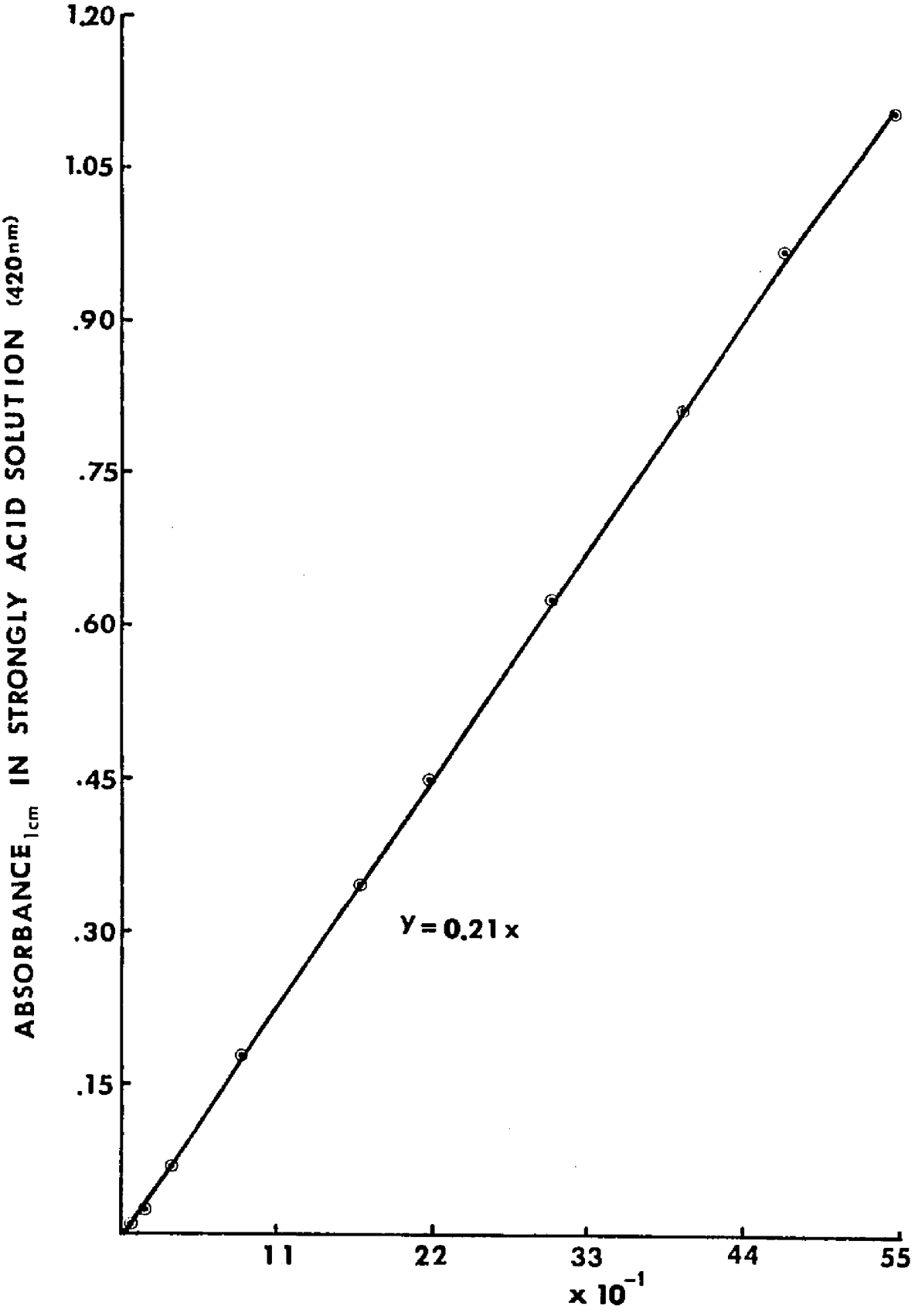

1.20
1.05
.90
.75
.60
.45
.30
.15
ABSORBANCE$_{1cm}$ IN STRONGLY ACID SOLUTION (420nm)
Y = 0.21 x
11
22
33
44
55
x 10^{-1}
CONCENTRATION IN TERMS OF ppm $SO_4^{=}$

FIGURE 5

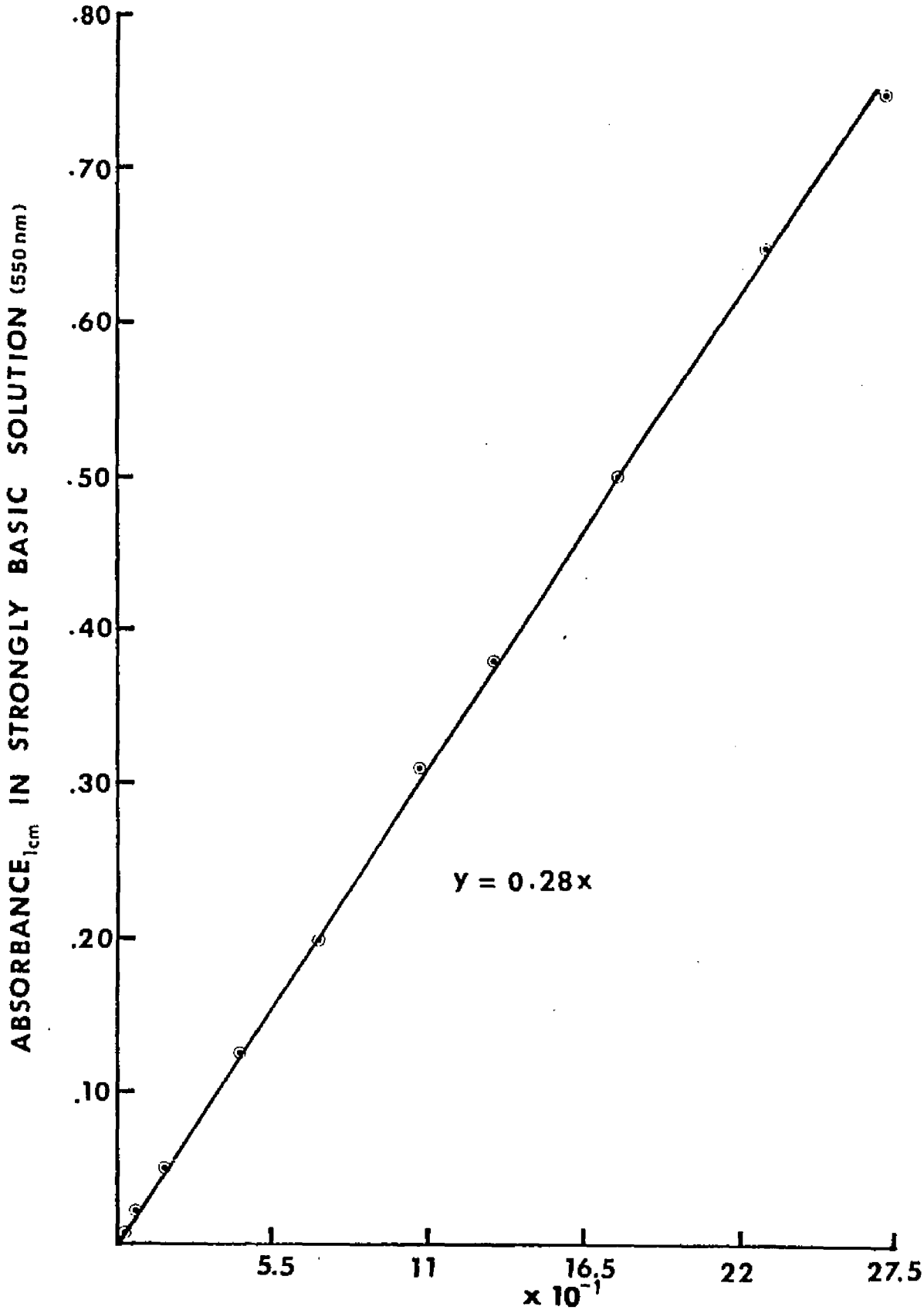

.80
.70
.60
.50
.40
.30
.20
.10
ABSORBANCE$_{1cm}$ IN STRONGLY BASIC SOLUTION (550 nm)
y = 0.28x
5.5
11
16.5
22
27.5
x 10^{-1}
CONCENTRATION IN TERMS OF ppm $SO_4^{=}$

FIGURE 6

the said amount). As mentioned before, all data were taken in sets of five and some representative standard deviations at various levels are given in Table II. The detection limit is normally defined to be twice the standard deviation of the blank, but in this case the blank itself was uniformly and reproducibly zero. (Procedure carried out with the addition of distilled water in lieu of sulfate solutions). Nominally 0.1 μg was the minimum detectible amount under such conditions, although the standard deviation at this level became as high as the value itself and was basically a function of instrument stability rather than the precision of the method itself.

III. REMARKS:

1. For an aqueous solution to be transferred effectively to a glass fiber filter, the microliter pipet tip must touch the spot wet with a water-miscible solvent with a low surface tension such that it wets the filter. The solvent chosen for this purpose was methanol. Glass fiber itself is very water repellent, aqueous solutions tend to 'bead' on it. If the original spot of methanolic PDA-bromide put on the filter became dry by the time transfer of the aqueous solution was attempted, the spot was remoistened with another drop of methanol. However, this was done only if necessary because it was advantageous to keep the diameter of the injection spot as small as possible.

2. Actually two separate sets of calibration curves were constructed to study the effect of volume of the injected solution. One set of calibration curves was constructed by varying the amount

TABLE II

PRECISION OF THE AQUEOUS SULFATE DETERMINATION PERIOD

AMOUNT OF SULFATE ON FILTER, μg	MEASUREMENT IN					
	ACID			BASE		
	MEAN ABSORBANCE	RANGE	% STANDARD DEVIATION	MEAN ABSORBANCE	RANGE	% STANDARD DEVIATION
0.56	0.011	0.010	14.8	0.015	0.011	11.8
1.39	0.029	0.013	8.3	0.038	0.018	8.4
3.46	0.070	0.019	4.6	0.097	0.027	4.4
8.67	0.182	0.048	4.3	0.243	0.044	2.8
10.0	0.211	0.030	2.4	0.280	0.052	3.1
21.7	0.457	0.104	3.9	0.610	0.141	4.0
54.2	1.14	0.210	4.1	1.53	0.350	4.1

(1 - 100 μl) of a standard sulfate solution placed on the filter and in the other set 100 μl of sulfate solutions of varying concentration was used. There was no discernible difference in the data obtained and therefore only one calibration plot is presented.

3. Injections of solutions up to 25 μl in amount was rapid and convenient. Amounts exceeding 25 μl were slow in transfer but the process could be facillitated somewhat by adding another drop of PDA-bromide at some halfway point during the transfer.

4. Reproducibility was improved, especially with the lower amounts, by allowing the spot to dry as completely as possible before chromatographing, this apparently allowed the PDA-sulfate to form and nucleate completely.

5. Ethanol could not be used as an eluting solvent because it reacted subsequently with nitric acid. Initial experiments with ethanol showed that gas pockets were formed in the filter when nitric acid was added to a filter moist with ethanol. At times, these pockets popped open with minor explosions liberating nitrogen dioxide, if gross amounts of ethanol were present. Apparently, ethyl nitrate was formed during the process. Methanol did not undergo a similar reaction with nitric acid, even after storage for months. Experiments done in collaboration with Dr. W. T. Burnett showed that the oxidation of methanol to formic acid and formaldehyde under such conditions was not very significant. A gas chromatographic analysis was done of the chloroform extract of a 1:1 methanol-nitric acid mixture after

keeping the later for a month at laboratory temperature.

6. Like water, nitric acid would not penetrate into a dry glass fiber filter. The filter had to be moist with methanol for the acid to be quickly distributed into the filter. If the filter became dry before the acid treatment it could be remoistened with methanol/acetone. Use of excessive amounts of methanol/acetone was avoided because if the acid became too dilute it took much longer to react, and precision decreased, possibly because a different product was introduced through side reactions.

7. Acetone generally undergoes an acid or base catalyzed aldol type condensation leading to the formation of diacetone alcohol and then to mesityl oxide. A mixture of 1:1 acetone and concentrated hydrochloric acid turned yellowish after $\sim$ 2 hours at room temperature. Interestingly enough even after keeping for 2 days, no change in color was observed when acetone was treated (1:1 mixtures) with either concentrated nitric acid or 1N sodium hydroxide. However, the possibility that these compounds might have formed in traces could not be overlooked. Because these compounds as well as acetone itself absorb strongly in the uv region, (methanol also absorbs in the uv but this absorption is almost at the edge of the uv - vacuum uv division), the decision was made to measure absorbance in the visible region. All PDA compounds (including its nitro derivatives) absorbed in the uv region as well, a fact that was used by Jones and Stephen[245] as the basis for an analytical procedure. The extinction co-efficients at the maxima, however, were comparable

to those in the visible region and even if such interferences could have been obviated, no significant gains would have resulted by measurement in the uv region. Furthermore, since ultimately the goal of the method was to determine airborne sulfates it was expected that organic material present in the air would be collected concommitantly and these might very well lead to interferences if measurements were made in the uv region.

8. Over 10 μg sulfate levels, it was not possible to remove every trace of color developed from the filter. However, apparently no significant amounts remained on the filters to affect the results adversely.

9. Glass fiber filters inevitably led to fibrous material in the solution and removal of the same before absorbance measurements was essential. The solution could have been filtered through a regular filter paper, but it was more convenient and rapid to use funnels with stems lightly packed with good quality glass wool. After each use the funnel was rinsed with acetone and the first 1 ml of the next solution filtered discarded.

10. Although data reported here do not show a significant superiority of one method over the other in regard to measurement in acidic or basic solutions, measurement in basic solution was preferred because of a) slight enhancement of sensitivity ($\sim 30\%$) b) no interference due to any oxides of nitrogen that might be formed during the nitration process and dissolved in the acid. There was another theoretical advantage in favor of measurement of basic solution - the extinction coefficient

exhibits a much higher degree of pH dependency at low pH values than at high pH values. As will be shown in Chapter XI no change in extinction coefficients was noted past pH 10; and then it became virtually pH independent. However, at the high concentrations of acid used, small variations in the amount of acid were also unlikely to cause any measureable cahnge in pH or shift of the equilibrium. At such concentrations ionic behavior, of course, is grossly non-ideal.

11. The calibration plots given in Figures 5 and 6 in this chapter may be represented respectively by the equations $y = 0.21\ x$ and $y = 0.28\ x$ respectively where y = absorbance and x = sulfate concentration in ppm in the measuring volume. Here the total measurement volume was 10 ml and because each mole of sulfate was associated with 2 moles of PDA leading to the formation of 2 moles of aminonitroperimidine, it can be easily calculated that a sulfate concentration of x ppm amounts to a concentration of $\frac{x}{0.48}$ μm aminonitroperimidine. If the factors 0.21 and 0.28 are multiplied with 0.48 the equations $y = 1.008 \times 10^{-2}x$ and $y = 1.344 \times 10^{-2}x$ are obtained where x = concentration of the aminonitroperimidine in micromolar units. These equations are virtually identical to the equations $y = 1.01 \times 10^{-2}x$ and $y = 1.35 \times 10^{-2}x$ presented for the Beer's law behavior of aminonitroperimidine in Figure 4 in the previous chapter.

This correlation establishes that:

a) under the conditions and amounts used for the reaction, the conversion of the sulfate salt of PDA to aminonitroperimidine

is quantitative;

b) the chromatographic removal process removes excess PDA-bromide successfully while retaining PDA-sulfate.

IV. RESULTS OF INTERFERENCE STUDIES:

Interference studies were carried out in detail only with selected anions, since the chemical basis of the method indicate that cationic interference would be unlikely. Interference studies were carried out to determine a) the percentage interference (in terms of increased absorbance from calibration value without interferant) imposed by the interferring ion on 10 micrograms of sulfate (100 μl, 100 ppm) where the former was present in amounts 10,000, 1,000, 100, 10 and 1 times the amount of the sulfate. b) the interfering threshold, i.e., with a 100 μl injection of the interferring ion in absence of sulfate the concentration at which color development on the filter was first detected.

The results of the study (all determinations were carried out in sets of five) are shown in Tables III and IV. If the mean of the results were within 5% of the mean calibration value without interferant, extent of interference is reported as none.

From the tables it can be readily ascertained that the method can be regarded as relatively interference free, at least as far as application to actual water samples are concerned. The only significant interferences were due to oxalate, phosphate, and bicarbonate. (Studies with carbonate could not be carried out because highly alkaline solutions such as sodium carbonate reacted

TABLE III

EXTENT OF INTERFERENCE ON AQUEOUS SULFATE DETERMINATION

100 µl 100 ppm sulfate injection, methanol elution

Interfering Ion	CONCENTRATION (TIMES THAT OF SULFATE) 1:1	1:10	1:100	1:1000
F^-	ND	NONE	NONE	NONE
Cl^-	ND	NONE	NONE	NONE
Br^-	ND	ND	NONE	NONE
I^-	ND	ND	ND	NONE
$HCOO^-$	NONE	NONE	50-100%*	ND
$C_2O_4^=$	133%	V.H.	V.H.	ND
CH_3COO^-	NONE	NONE	16.5%	ND
$H_2PO_4^-$	33%	V.H.	V.H.	ND
HCO_3^-	11%	V.H.	V.H.	ND
NO_3^-	NONE	NONE	V.H.	ND

ND = not done, V.H. = very high, > 500%

*irreproducible

TABLE IV

THRESHOLD CONCENTRATIONS AT WHICH INTERFERENCE FIRST APPEARS

100 µl Injection, Methanol Elution

INTERFERING ION	THRESHOLD CONCENTRATION
Cl^-, Br^-, I^-, F^-	Saturated Sodium/Potassium Salt solutions do not interfere.
$HCOO^-$	> 1000 ppm
$C_2O_4^=$	Interferes at all levels studied, down to 10 ppm
CH_3COO^-	> 5000 ppm
$H_2PO_4^-$	> 25 ppm
HCO_3^-	> 100 ppm
NO_3^-	> 1000 ppm

with PDA-salts liberating the free amine in an equilibrium process; the free amine was rapidly oxidized by air. For the same reason the method was inapplicable to samples with pH higher than 9 without pretreatment.)

Studies were then carried out with an eluting solvent of 1% monochloroacetic acid in methanol to see if this solvent reduced the interference. A separate calibration curve was constructed with this particular eluting solvent and is shown in Figure 7. The precision was in general poorer than that with methanol. Standard deviation was acceptable (< 10%) at levels over 10 μg but severely deteriorated at lower and lower levels; at levels between 5 and 10 μg the standard deviation was between 10 and 20% and unusably erratic at levels 1 μg and below. Results of the interference study is shown in Tables V and VI.

As the data show, some improvement was observed but it was doubtful that whether any actual situation would be encountered in which this solvent would lead to more reliable results than those obtained with methanol.

V. APPLICATION TO ACTUAL WATER SAMPLES:

Thoma[483] conducted a study involving sulfate analyses of a number of water samples by various methods to compare them with the results obtained by the PDA-sulfate pyrolysis method developed by her. Some of these samples were still available and were subjected to analysis by the method described in this work (100 μl aliquots and measurements in base were used). All values other than those obtained by this method are quoted from Thoma's

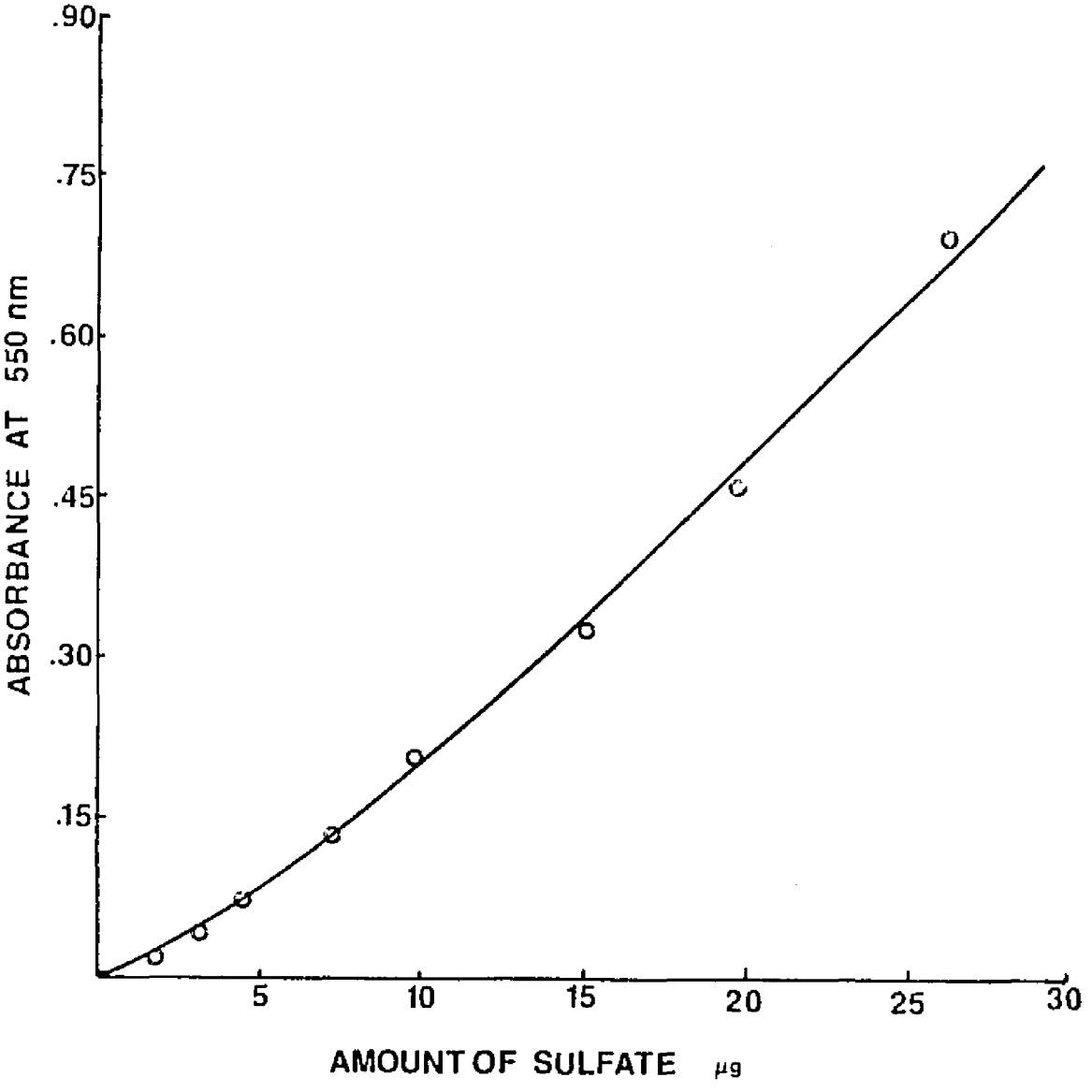

.90
.75
.60
.45
.30
.15
ABSORBANCE AT 550 nm
5
10
15
20
25
30
AMOUNT OF SULFATE µg

FIGURE 7

TABLE V

EXTENT OF INTERFERENCE ON AQUEOUS SULFATE DETERMINATION

100 μl 100 ppm Sulfate injection, MCAA Elution

INTERFERING ION STUDIED	CONCENTRATION (TIMES THAT OF SULFATE) 1:1	1:10	1:100	1:1000
Cl^-, Br^-, I^-, F^-	ND	ND	ND	NONE
$HCOO^-$	ND	NONE	NONE	ND
$C_2O_4^=$	40%	~750%	V.H.	ND
CH_3COO^-	NONE	NONE	20%	ND
$H_2PO_4^-$	25%	340%	V.H.	ND
HCO_3^-	NONE	37%	475%	ND
NO_3^-	NONE	NONE	30%	ND

ND = not done V.H. = very high, greater than 750%

TABLE VI

THRESHOLD CONCENTRATIONS AT WHICH INTERFERENCE FIRST APPEARS

100 µl Injection, MCAA Elution

INTERFERING ION	THRESHOLD CONCENTRATION
Cl^-, Br^-, I^-, F^-	Saturated sodium/potassium salt solutions do not interfere
$HCOO^-$	> 5000 ppm
$C_2O_4^=$	> 25 ppm
CH_3COO^-	> 5000 ppm
$H_2PO_4^-$	> 50 ppm
HCO_3^-	> 500 ppm
NO_3^-	> 1000 ppm

dissertation. The data are presented in Table VII along with uncertainties for a 95% confidence limit ($\pm 2\sigma$).

The data show that the results obtained by the current method correlate well with the standard methods (barium sulfate gravimetry and turbidimetry) as well as Thoma's method and, within reasonable degree, to the barium-chloranilate method. The PDA-sulfate nephelometric method generally produced values far higher than those obtained by other methods, and a detailed discussion of this has been given by Thoma.[483]

The salient point is that results that are almost equally reliable may be obtained by the current method at a fraction of the time used for other methods. The current method takes about half an hour for a single determination and an hour for 10 simultaneous determinations.

TABLE VII

COMPARISON OF ANALYTICAL RESULTS OBTAINED BY DIFFERENT METHODS

SULFATE (ppm)

Sample	pH	$(PDA)_2SO_4$ Pyrolytic Method	$BaSO_4$ Gravimetric	$BaSO_4$ Turbidimetric	Barium Chloranilate	$(PDA)_2SO_4$ Nephelometric	This Work
Baton Rouge, La.	8.67	10.4 ± 0.5	9.8	10.4 ± 0.3	6.96 ± 0.19	43.2 ± 7.3	10.8 ± 0.8
Garnavillo, Ia.	7.86	11.3 ± 1.9	12.6	13.6 ± 0.2	13.24 ± 1.04	71.0 ± 2.4	12.8 ± 1.0
Kenner, La.	9.61	54.9 ± 1.9	52.8	54.4 ± 0.8	46.8 ± 0.84	61.2 ± 0.3	53.0 ± 1.9
Natchitoches, La.	7.32	48.4 ± 0.5	43.6	45.2 ± 0.4	41.20 ± 0.99	42.0 ± 1.0	46.0 ± 1.1
Diamondhead, Miss.	8.67	8.2 ± 0.3	9.1	9.5 ± 0.1	7.60 ± 0.40	19.8 ± 0.5	9.1 ± 2.2

CHAPTER IX

THE DETERMINATION OF AEROSOL SULFURIC ACID AND ITS SPECIATION FROM AMMONIUM SULFATE

I. CALIBRATION WITH AEROSOL SULFURIC ACID

Thomas[487] reported that the amount of aerosol sulfuric acid collected on a filter was linear with time with the generator described by Thomas, et al.[486] Aspirating a 980 ppm sulfuric acid solution Thomas established that the collection rate was about 20 μg/min at the constant sampling rate provided by the Gelman filter tape sampler (~ 18 liters/minute). For this work this collection rate was regarded to be far too high and a rate of about an order of magnitude lower was desirable. The concentration of sulfuric acid aspirated was therefore reduced to 100 ppm retaining other parameters such as fuel pressure, air pressure, diameter of aspiration tube constant (1.0 psi, 12.5 psi and 1 mm diameter teflon respectively). Five minute samples were collected at 10 liters/minute on PDA-bromide impregnated filters (impregnated after Thomas, et al.'s method,[488] 10 ml of 1.8% methanolic PDA-bromide poured on a ~ 100 mm diameter filter kept in a petri dish and dried at 80°C for 30 minutes) and analyzed by the PDA-sulfate Pyrolytic method, monitoring the sulfur dioxide evolved with a total sulfur monitor (TSM). Triplicate samples were analyzed and the mean was found to be somewhat lower than 10 micrograms of sulfate. Because it was beyond the scope of this study to investigate the exact relationship between the concentration of generated aerosol sulfuric acid and the sulfuric acid concentration of the aspirated solution, the sulfuric acid concentration was increased simply by trial until 5 minute samples collected resulted in a mean average collection of ~ 10 μg sulfate

as determined by the pyrolysis-TSM method (set of five samples, mean 10.1 μg, range 2.1 μg, standard deviation 4.9%). The concentration of the sulfuric acid solution aspirated was later determined by acidimetry to be 113.8 ppm. A set of eight samples were collected, three analyzed by the Pyrolysis-TSM method and five by the method developed in this work, heretofore to be referred to as the nitration method. Eleven different collection times were used for the collection of samples: 30 sec., 48 sec., 72 sec., 1.5 min., 2 min., 2.5 min., 5 min., 7.5 min., 10 min., 12.5 min. and 15 minutes. A total number of eighty-eight samples were thus obtained. The peaks in the recorder traces of the total sulfur monitor were integrated using a manual planimeter to yield the peak area and the latter was calibrated by using a triplicate set of 10 μg aqueous sulfate samples (100 μl, 100 ppm) put on identically impregnated filters. The formation of sulfur dioxide from the aqueous samples were assumed after Maddalone[311] to be quantitative.

Samples collected for analysis by the nitration method were collected on filters that were impregnated differently from Thomas, et al's procedure. A 72 mm x 72 mm square was cut out of the 102 mm diameter glass fiber filter. A ~ 20 mm wide impregnation band was created on this piece by applying 1 ml of 3% methanolic PDA-bromide solution containing 0.02% butyl hydroxy toluene (BHT) with a disposable pipet as evenly as possible starting at ~ 10 mm from the bottom of the piece. The impregnated region contained 2.1 mg PDA-bromide/cm^2, roughly the

same as the amount recommended by Thomas[487] for optimum collection and analysis. After drying for a half hour at 80°C the piece was cut into strips wide enough to fit in the Gelman Sampler (~ 18 mm) and to cover the entire sampling area. Each strip thus had a ~ 20 mm wide impregnated region approximately 10 mm from the bottom and the top of this band was left unimpregnated. The reason for choosing such an impregnation geometry was to make subsequent chromatographic removal of the excess PDA-bromide feasible and facile. The strips were chromatographed, five at a time with methanol as the eluting solvent, as described in the previous chapter. The strips were placed in the beaker for a period of 15 minutes rather than 10 minutes as was used for aqueous samples because of the much larger amounts of excess reagent present. The addition of butyl hydroxy toluene inhibits the decomposition of PDA and was added as a precautionary measure because the temperature of the sample stream coming from the stack generator was fairly high. The sample spot was cut away by a 16 mm diameter filter cutter and measurment was made in basic solution at 550 nm following the treatment procedure described in the previous chapter.

The results of the analyses are shown in Table VIII. Absorbance values obtained in the nitration method are plotted against the amount of sulfate found by the Pyrolysis-TSM method in Figure 8.

II. REMARKS

The results in Table VIII shows that the nitration method correlated well with the pyrolytic method and was probably somewhat

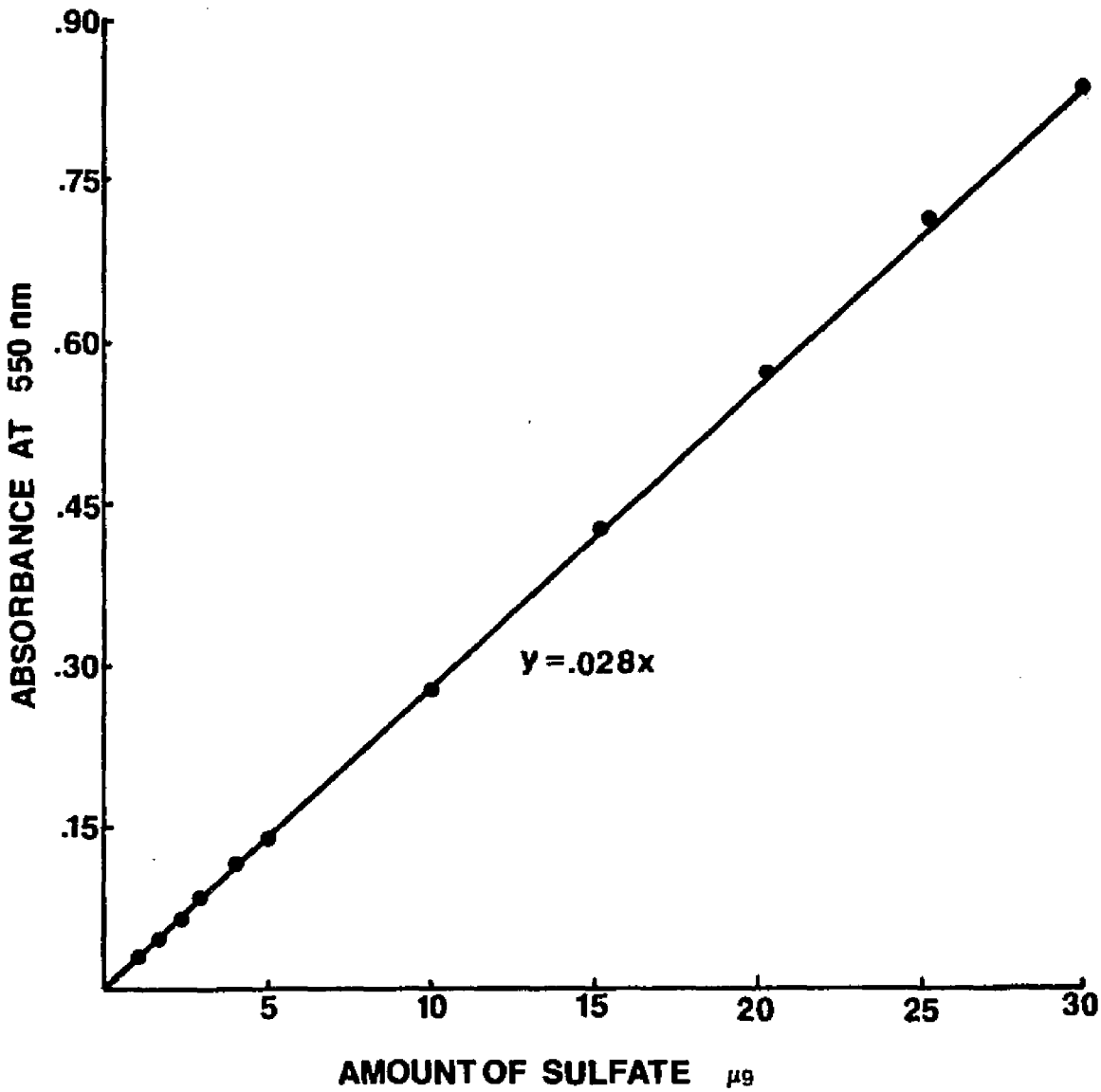

.90
.75
.60
.45
.30
.15
ABSORBANCE AT 550 nm
y = .028x
5
10
15
20
25
30
AMOUNT OF SULFATE μg

FIGURE 8

TABLE VIII

RESULTS OF AEROSOL SULFURIC ACID DETERMINATION

PYROLYTIC-TSM vs. NITRATION METHOD

Group	Sampling Time	Sulfate found by Pyrolysis-TSM Method µg	% SD	Absorbance (A^{1cm}_{550nm}) obtained in the nitration method	% SD
1	30 S	1.0	10.1	0.026	8.3
2	48 S	1.7	8.9	0.044	7.6
3	72 S	2.4	9.2	0.065	7.4
4	1.5 m	3.1	8.7	0.085	5.9
5	2.0 m	3.9	10.8	0.114	5.0
6	2.5 m	5.0	8.8	0.138	5.1
7	5.0 m	10.1	7.8	0.276	4.2
8	7.5 m	15.2	5.9	0.422	4.8
9	10.0 m	19.9	6.8	0.564	5.0
10	12.5 m	25.3	10.0	0.702	6.1
11	15.0 m	30.0	4.5	0.838	5.3

more precise. It is hard to comment on the relative precision since the uncertainty in the sampling step itself must also be considered.

The calibration plot given in Figure 8 in terms of the pyrolytic method as the reference method clearly established that the calibration was identical to that obtained for aqueous sulfate. The calibration equation obtained here was $y = 0.028x$ where y = absorbance and x = amount of sulfate in micrograms which is equivalent to the calibration curve obtained for aqueous sulfate $y = 0.28x$ where x = sulfate concentration in parts per million in a measuring volume of 10 ml.

Impregnated filters do not keep well very long, even in a desiccator. They should be used within 48 hours after preparation.

III. SPECIATION FROM AMMONIUM SULFATE

It is obvious from the extensive discussions carried out in the first part of this dissertation, that a truly meaningful specific determination of aerosol sulfuric acid should be able to differentiate it from ammonium sulfate; because the latter is in general the dominant component of aerosol sulfate burden of our air and in terms of hazardous consequences it is not as damaging as sulfuric acid. As has been mentioned in Chapter III, no toxicologic data are available on ammonium bisulfate or any other sulfate and bisulfate salts of importance except zinc sulfate and zinc ammonium sulfate. It is unlikely that the last two compounds are present in the ambient air to any significant extent except under special circumstances (cf. Donora, 1948) but based

on an educated guess, ammonium bisulfate probably poses a hazard index equivalent to that of sulfuric acid. In the absence of toxicologic data, no attempts were made to differentiate sulfuric acid from ammonium bisulfate, although theoretically the concept of the speciation process developed here could easily be extended to separate ammonium bisulfate.

As has been mentioned before, PDA-bromide reacts topochemically with the sulfuric acid aerosol because the later exists as a liquid aerosol under all measurable relative humidity conditions. Other airborne sulfate salts on the other hand exist as solid or liquid aerosols depending on the prevailing relative humidity (R.H.). As long as the prevailing R.H. is below the critical humidity of the species under consideration it is present as a solid aerosol and will not react with the PDA-bromide upon sampling to form PDA-sulfate. This, however, does not in itself constitute a speciation method since although the material does not react with the PDA-bromide it is impacted on the filter and leads to interferences in both the pyrolytic and the nitration methods. In the pyrolytic method ammonium sulfate decomposes to form sulfur dioxide at the pyrolysis temperature employed for the decomposition of PDA-sulfate and in the nitration method ammonium sulfate is sufficiently soluble in methanol to react subsequently with PDA-bromide to form PDA-sulfate during the chromatographic elution process. If, however, the unreacted soluble sulfate could be converted to some other very insoluble salt, a method of speciation could be achieved. The obvious choice

for a very insoluble salt is barium sulfate, which is in fact more insoluble than PDA-sulfate. The formation of barium sulfate from ammonium sulfate in the presence of PDA-sulfate must meet the following criteria:

a) the barium sulfate must be formed from the ammonium sulfate without significant formation of PDA-sulfate

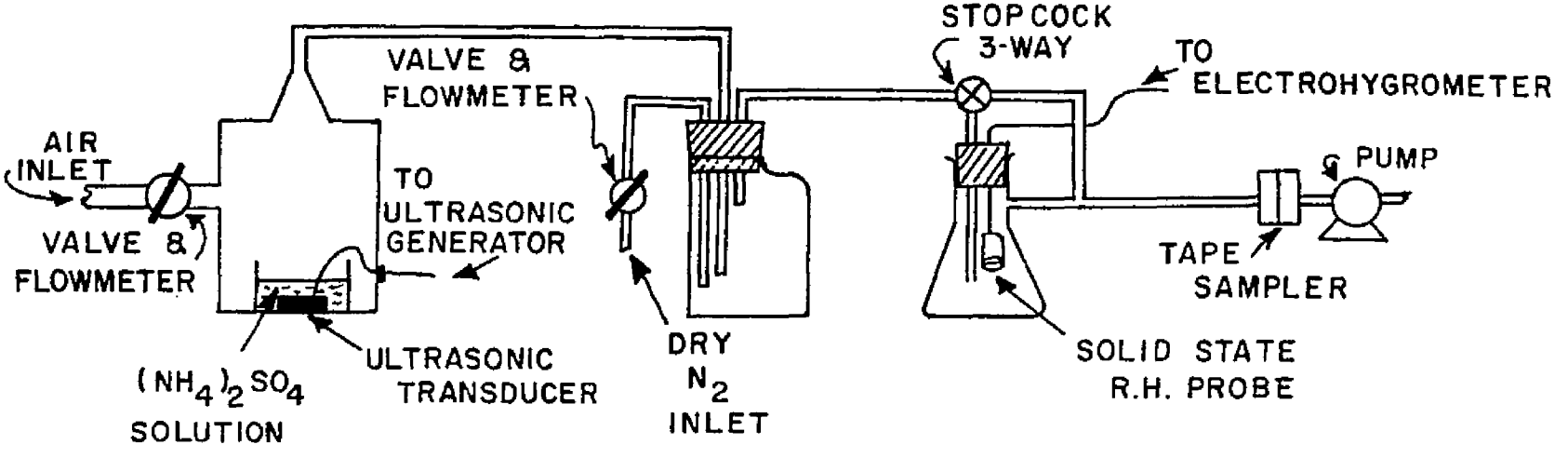
b) the PDA-sulfate already present should not metathesize to barium sulfate the latter being the more insoluble salt.

The second criterion is not difficult to meet, since normally a metathesis reaction with a highly insoluble compound proceeds only slowly and rather drastic conditions (boiling, etc.) are normally necessitated (cf., determination of sulfate involving indirect titrimetric methods, Chapter IV). To meet the first condition, however, the solvent containing the barium ion must be of sufficiently low dielectric constant such that it does not significantly ionize PDA-bromide yet provides a significant barium ion activity. A saturated solution of barium acetate in a methanol-acetone mixture of various compositions was studied to test the hypothesis.

Ammonium sulfate aerosol cannot be generated by the stack generator because the latter actually generates aerosol by a combustion process. An ultrasonic generator was used to generate ammonium sulfate aerosol and the sampling set up is shown in Figure 9. A 200 ppm ammonium sulfate solution was agitated by a high energy high frequency transducer to generate ammonium sulfate aerosol in the form of a fine mist. The sample was drawn

FIGURE 9

CONTROLLED HUMIDITY AMMONIUM SULFATE AEROSOL GENERATOR



from a height $\sim$ 20 cm above the solution surface into a four liter polyethylene mixing chamber where dry nitrogen was introduced from a tank via a valve and flowmeter to reduce the relative humidity (R.H.) of the sample prior to sampling. The R.H. of the stream coming directly from the aerosol generator was virtually 100%, and therefore the flow rate was adjusted to about one and one half times the flow rate through the aerosol generator, to reduce the R.H. of the sample stram to $\sim$ 40%. The sample stream was drawn through the sampling filter incorporated in the Gelman tape sampler either directly or through a one liter erlenmeyer flask in which a solid state humidity probe was installed. By means of a three-way stopcock the sample stream could be made to flow through the flask or bypass it. The R.H. was monitored prior to sampling by directing the flow through the flask and when the R.H. was satisfactorily adjusted to 40 $\pm$ 5% by controlling the dry flow, the flask was bypassed and sampling began. Ammonium sulfate has a critical deliquescence point of 81%[522] and so at a R.H. of 40% it was present as a solid particulate. The nominal flow rates used were 1.0 liter/minute through the aerosol generator and 1.5 liters/minute of dry nitrogen into the mixing chamber. Five minute samples were collected on band-impregnated filter strips as described in the previous section and triplicate sets were analyzed by Thomas, et al.'s total sulfate pyrolytic method and by the nitration method. The respective mean values obtained were 8.5 μg and 8.9 μg and the relative standard deviations were 11.8% and 9.9% respectively.

It would seem that this relatively high deviation reflected the somewhat imprecise nature of the aerosol generation and sampling process rather than the precision of the analytical procedures used. With the pyrolytic method the area surrounding the sample spot was cut away with a 16 mm dia. filter cutter before treatment with a methanolic PDA-bromide solution and subsequent pyrolysis; the PDA-bromide solution converted the ammonium sulfate to PDA-sulfate. With the nitration method, chromatography was carried out as described in the previous section, following which the area surrounding the sample spot was cut out by a 16 mm. diameter filter cutter and analyses performed as described earlier.

For the ammonium sulfate interference removal study the sampled area was treated with five drops of saturated barium acetate solution in a methanol acetone mixture of various compositions and allowed to dry before analysis was carried out either by the pyrolytic or by the nitration method. Triplicate samples were analyzed in each case. The results of the study with various solvent compositions are shown in Table IX.

IV. RESULTS

As the results show, the studies indicated that the optimum solvent composition lies somewhere between 40 and 10% methanol. Acetone-methanol mixtures containing 25 and 30% methanol (by volume) were therefore next investigated and it was apparent that a 75% acetone-25% methanol mixture was the best choice and such a treatment virtually removed all ammonium sulfate as barium sulfate.

TABLE IX

AMOUNT OF SULFATE FOUND ON FILTER AFTER TREATMENT WITH A SATURATED BARIUM ACETATE SOLUTION IN A METHANOL-ACETONE SOLVENT SYSTEM

GROUP	VOLUME % METHANOL IN SOLVENT	PYROLYTIC METHOD Mean	% SD	NITRATION METHOD Mean	% SD
1	no treatment	8.5	11.8	8.9	9.9
2	100	8.6	11.2	7.8	13.1
3	80	6.3	10.8	6.6	11.4
4	60	2.1	12.4	1.8	10.6
5	40	1.5	8.6	1.0	6.5
6	20	0.56	11.1	0.54	12.1
7	10	2.9	10.8	3.1	10.1
8	0	8.8	11.7	9.0	9.5
9	25	0.30	14.5	0.12	20.1
10	30	0.59	13.8	0.73	15.6

V. REMARKS

The above results still did not establish whether the barium acetate solution so applied to a filter that already contains PDA-sulfate formed through the reaction with sulfuric acid would attack the PDA-sulfate forming barium sulfate. A study of both sulfuric acid and ammonium sulfate aerosols collected on the same filter was therefore necessitated. Further it was realized that in actual field sampling situations it would be impractical to dilute sample streams with dry air to control humidity. At this point the concept of controlled heating of the sample stream for humidity control was conceived.

VI. REMOVAL OF AMMONIUM SULFATE IN THE PRESENCE OF PDA-SULFATE

Concurrent sampling of ammonium sulfate and sulfuric acid aerosols and controlling of the sample stream at the same time proved impossible without adding massive amounts of dry nitrogen to the system to reduce humidity. By virtue of the very nature of the respective generation processes, aerosol sulfuric acid generated by the stack generator and aerosol ammonium sulfate generated by the ultrasonic generator were both highly humid. Further, the acid aerosol stream was hot ($\gtrsim 100^{\circ}C$) and the addition of dry nitrogen resulted in a lowering of temperature which would have actually increased the relative humidity, were it not for the dilution caused by the dry nitrogen.

The idea of simultaneous generation of ammonium sulfate and sulfuric acid by the ultrasonic generator was discarded because it was obvious that there would be no easy way of establishing the

identity of the actual species generated.

The devised method of study was therefore a compromise, involving successive sampling but it was felt that it did not significantly alter the problem actually encountered in field sampling situations, i.e., the problem of speciating ammonium sulfate and sulfuric acid. The acid aerosol was sampled first and then the ammonium sulfate was collected on the same filter. The reverse process did not work because as had been mentioned before. The relative humidity of the acid aerosol stream was very difficult to control because of its relatively high temperature. If this highly humid stream was sampled after the ammonium sulfate collection, the latter (although originally collected as a solid particulate) seemingly began to react with the filter.

The filter tape sampler was set up in such a fashion that connections to the ultrasonic generator or the stack generator could be rapidly interchanged. The same set-up as described in the first section was used to sample the acid aerosol. The humidity of the ammonium sulfate aerosol stream from the ultrasonic generator was controlled differently, with field sampling in mind. A 9 mm i.d. stainless steel tubing 20 cm in length was connected between the sampler and the aerosol generator, the physical location being immediately prior to the sampler. A heating tape (100W @ 120 V) was wrapped around the tube and connected to a powerstat. By varying the setting of the powerstat the heating of the sample stream and therefore its temperature and relative humidity could be controlled. Excessive heating was

avoided because such heating could have adversely affected sample stream compositions and would have probably caused PDA-bromide decomposition leading to interferences.

Five minute samples at 1 liter/minute collection rate were collected and subjected to the barium acetate treatment and then analyzed by the nitration method. From the data shown in Table X it may be seen that under this particular experimental set-up and at the cited flow rate, a setting of 40 on the powerstat was adequate for the conversion of the ammonium sulfate from a liquid to a solid aerosol.

Successive sampling was attempted. A set of fifteen band impregnated filter strips was used to collect 10 μg samples of the acid aerosol (5 minute collection time, all other parameters were the same as described in section I). Six strips were removed after sampling and analyzed by the nitration method, three after barium acetate treatment and three without treatment. As in the case of the other samples, dry nitrogen was drawn through the filter for 1 minute to remove any excess moisture from the filter and then the connection was switched to the heated ammonium sulfate aerosol stream and sampled for 5 minutes. The samples were stored in a desiccator prior to analysis, generally conducted in a batch. Analysis had to be done within 24 hours of sampling, longer intervals led to erratic results. Three of the samples were analyzed by the nitration method without further treatment, and the rest were subjected to the barium acetate treatment and half of this batch subjected to analysis by the pyrolytic method

TABLE X

CONTROL OF HEATING PARAMETER TO CONVERT AMMONIUM SULFATE FROM A LIQUID TO A SOLID AEROSOL

POWERSTAT SETTING	AMOUNT OF SULFATE FOUND BY THE NITRATION METHOD AFTER BARIUM ACETATE TREATMENT, μg.
0	8.8
10	9.0
20	8.9
30	2.6
40	0.1
50	0.1
60	0.1

100 watt heating tape wrapped around 20 cm x 9 mm i.d. S.S. tubing
Flow rate 1 liter/minute

and the rest by the nitration method. A further set of six samples were used to collect only ammonium sulfate under these conditions. Three of these samples were analyzed after the barium acetate treatment and the other three without treatment, both by the nitration method. The results are reported in Table XI.

VII. REMARKS

1. Barium acetate was chosen over other barium salts because of its high solubility in alcoholic solvents. It is possible that a more exotic compound such as barium iodide would have been better. The success of the interference removal procedure, however, leaves little to be desired in this regard.

2. Some degree of care is necessary in applying the barium acetate solution, especially when using the nitration method. Excessive spreading towards the bottom of the strip results in PDA-bromide leaching to this region which subsequently contaminates the solvent during chromatography and thus separation becomes impossible.

3. Strictly speaking, adjustment of the heating parameter has been done on an arbitrary basis, theoretically a sample stream at 20°C and 100% relative humidity (R.H.) can be reduced to 80% R.H. by heating it to only 24°C. Equilibriation however, is a slow process and such calculations are not very meaningful for achieving liquid to solid aerosol conversion at realistic flow rates. Because such conversion processes normally exhibit a hysteresis pattern,[96] the R.H. must be substantially lower than the critical deliquescence point. A R.H. of 40% without a doubt

TABLE XI

STUDY OF THE AMMONIUM SULFATE INTERFERENCE REMOVAL METHOD IN THE PRESENCE OF COLLECTED AEROSOL SULFURIC ACID

GROUP	DESCRIPTION	BARIUM ACETATE TREATMENT	ANALYSIS METHOD	RESULT Mean, μg	% SD
1	H_2SO_4 alone	Yes	Nitration	9.8	4.4
2	H_2SO_4 alone	No	Nitration	10.1	4.2
3	$H_2SO_4 + (NH_4)_2SO_4$	Yes	Nitration	10.3	6.2
4	$H_2SO_4 + (NH_4)_2SO_4$	Yes	Pyrolytic	10.8	9.8
5	$H_2SO_4 + (NH_4)_2SO_4$	No	Nitration	19.1	9.9
6	$(NH_4)_2SO_4$ alone	No	Nitration	8.8	8.9
7	$(NH_4)_2SO_4$	Yes	Nitration	0.15	20.1

provides a sufficient margin of safety in the case of ammonium sulfate which has a critical deliquescence point of 81%. For an inlet stream with a given moisture content at a given temperature the R.H. of the exit stream after heating can easily be calculated by monitoring the temperature of the exit stream. In the particular set-up used for this study, temperature/R.H. monitoring of the stream immediately after the heating tube may not have led to usable results since the stream still had to travel at least 20 cm before reaching the filter and some cooling must take place in the process and thus increase the R.H..

4. For actual field sampling, monitoring of the stream temperature immediately following the filter will probably be the best arrangement. After an initial measurement of ambient temperature and R.H., a quick calculation can be made to ascertain temperature to which the sample stream must be heated (if necessary) to reduce the R.H. to 40%. The temperature of the filtered stream can then be monitored by a thermistor, part of a feedback circuitry that controls the voltage applied to the heating elements (basically the same circuitry used for a constant temperature bath), with provisions for specifying the desired temperature.

5. The results reported in this chapter clearly establish that the prescribed method for removing ammonium sulfate interference in the specific determination of sulfuric acid can be successfully applied in the case of successively collected samples of the two species on the same filter. Logically, and with the present status of scientific knowledge, there is no reason to believe that

this method will not work in actual sampling situations. Different and more sophisticated heating arrangements, however, will probably be necessary for high volume sampling because at such high flow rates attainment of equilibrium through proper heat distribution in a turbulent stream are likely to be more difficult.

6. In all cases when sampling was conducted from the stack generator, a slightly reddish discoloration of the filter was observed. The colored compound was removed along with PDA-bromide during chromatography and did not cause any interference. The possible significance of this observation will be discussed in the discussions section.

CHAPTER X

EXTENSION TO THE RING OVEN, DETERMINATION OF SULFATE AT NANOGRAM LEVELS

The ring oven is a simple inexpensive device designed specifically for microanalysis. A detailed description of the apparatus and techniques are available in the monograph by Weisz[523] and its applications to air pollution studies have been eloquently presented by West.[528]

The ring oven technique is extremely sensitive but accurate quantitation requires some skill. Quantitation of unknown samples is generally carried out by visual comparison with standard rings. The procedure described here was based on the nitration method outlined in Chapter VIII. The detection limit on the ring oven by this method is 5 ng sulfate, and the working range was from 20 ng to 1 μg. There are, at best, only two reported methods that can claim sensitivities of these orders. The first one was a ring oven method also and is based on the barium-rhodizonate reaction and therefore was subject to all the errors and interferences involved with the precipitation of barium sulfate. The second employs the flame photometric detector and requires expensive instrumentation. The method reported herein is not intended to be 'just another method' that is sensitive, but a method that combines sensitivity and specificity, is free from interferences by common cations and from virtually all important anions present in realistic concentration, except oxalate.

I. Procedure: To successfully apply the ring oven technique to determine sulfate at trace levels, pre-cleaning of the glass fiber filters was absolutely necessary. According to the manufacturer's specifications, the glass filber filters used in this study (Gelman

spectrograde-A) contain substantial amounts of sulfate. The manufacturer's specifications guarantee no more than 2 μg sulfate/cm^2 of filter. In actual practice the batches of filters used during the course of this work were found to contain substantially smaller amounts, somewhere between 50 and 200 ng sulfate/cm^2 of filter as measured by the nitration method. The data reported in Chapters VIII and IX were also obtained using pre-cleaned filters when working at or below the 1 μg level. All other data were obtained without pre-cleaning. At the levels of determination possible and practical by the ring oven, the blank values obtained directly from the glass fiber filters without pre-cleaning were far too high to permit meaningful measurements.

To pre-clean, 102 mm diameter glass filber filters were cut in half and twenty such pieces were cleaned at one time by immersing them in 400 ml of a mixture of 50% ethanol and 20% HCl and 30% water and boiling for 4 hours at low heat. The solution was then decanted, washed thrice with 50 ml portions of ethanol and finally twice with 50 ml portions of acetone and then dried in an oven at 80°C.

Strips of the same dimension as described in Chapter VII were then cut out with a freshly unwrapped surgical scalpel blade. The amount of cleanliness and care necessary to conduct analysis at this level cannot be overemphasized; especially since measurable amounts of particulate sulfate are present in the

laboratory air.*

To prepare standard rings, 10 μl of sample volume, ranging in concentration from 0.5 ppm to 100 ppm were put on filter strips by the technique discussed in Chapter VIII. Two drops of 1% methanolic PDA-bromide solution was used to premoisten the spotting region and two further drops were added at the end of the sample injection. The filter strip was allowed to dry completely before chromatography and then chromatographed for 15 minutes, dried and the area surrounding the sample spot was cut away with a 16 mm diameter filter cutter. The filter was then lightly moistened with methanol and exposed to nitric acid vapors for two minutes, using a pair of plastic forceps to hold it just at the edge. It was then exposed to ammonia vapor for one minute and placed on a Whatman No. 41 filter paper prepositioned on the heating block of a ring oven and held in place by a retaining ring. (Because of its highly fibrous and non-uniform constitution ring oven work cannot be carried out directly on glass fiber substrate and direct impregnation of PDA-bromide on filter paper cannot be carried out because the later retains PDA-bromide too tenaciously to be eluted by a reasonable volume of any solvent.) The maximum aperture of the ring oven was used,

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*1000 l. samples of laboratory air sampled during August 1977 (when a concurrent situation of high humidity prevailed in the building) showed sulfate loading of the air in this building to be as high as 12 $\mu g/m^3$. It is possible that part of this resulted from the evaporation of water from the air conditioning duct drippings - these contained about 10 ppm sulfate.)

with the particular ring oven used, this opening was 33 mm in diameter. The small filter was centered on the ring oven as best as possible. The heating block temperature was maintained at $\sim 100^{o}C$. The colored material on the filter was eluted to the ring zone with six successive 25 µl aliquots of acetone, waiting between each addition to let the solvent evaporate.

II. Interferences: At the 10 ppm sulfate level, no significant change in color intensity from standard was observed from 100 ppm calcium, magnesium, iron (III), iron (II), bicarbonate, nitrate, acetate, formate, chloride, bromide, fluoride, and iodide ions concommitantly added to the sulfate solution. Phosphate did not interfere below 10 ppm; between 10 and 50 ppm the interference was minor and erratic but at the 100 ppm level severe interference was observed. Oxalate interfered at all levels studied, all the way down to 5 ppm. Of course, high levels of oxalate are not likely to be of common occurrence.

III. Results of Analyses of Actual Samples

The samples analyzed by the spectrophotometric method in Chapter VIII were subjected to study by the ring oven method. Only 2 µl sample aliquots were used, to test how well correlations could be made with the very small amounts of sulfate put on the filter. In every case it was possible to judge the sulfate concentration of the sample within $\pm$ 30% of the value obtained by the spectrophotometric method. With a more elaborate set of standard rings and a low power comparison microscope, possibly even more accurate judgements could be made.

CHAPTER XI

NITRO SUBSTITUTED 2-AMINO PERIMIDINES

SYNTHESIS, SEPARATION, STRUCTURES AND SOME PROPERITES

I. SYNTHESIS

Since PDA-bromide and PDA-sulfate apparently produced the same intense color upon treatment with concentrated nitric acid, it was thought that the same compound was being produced in both cases. Because PDA-bromide was more readily available, it was used to prepare milligram quantities of the compound of interest so as to establish its identity. Earlier, thin layer chromatography (TLC) on pre-coated plates was carried out on the material formed on the glass fiber filters (by removal of the latter by leaching with acetone, concentrating by evaporation and spotting on the TLC plate) through development with 1:1 cyclohexane:ethyl acetate. Only one spot was visible and therefore, it was concluded that the reaction product of PDA-sulfate and concentrated nitric acid on the filter medium in the trace quantities involved was a single pure species. There was no reason to believe that PDA-bromide under the same condition would give rise to any other product.

Reacting gram quantities of solid PDA-bromide with concentrated nitric acid produced a dark brown solution which on dilution with water yielded a flocculent precipitate. The color of the precipitate varied within different shades of orange in different synthetic batches and also elemental analysis of the product (after filtration, thorough washing with water and drying) yielded widely different elemental compositions. It was obvious that a number of compounds were being formed under these conditions, the ratio of the different components apparently varying from

batch to batch.

Thin layer chromatography on the products from different batches confirmed this conclusion. In one particular case as many as ten different components could be discerned. Virtually all of the color intensity was, however, concentrated in five spots, apparently indicating five principal products of the reaction.

In an effort to simulate the reaction conditions on the filter a solution of ~ 1 g. PDA-bromide in 100 ml water was treated with 100 ml concentrated nitric acid. White PDA-nitrate precipitated immediately and slowly started turning yellow through an intermediate green color. The reaction was proceeding very slowly and it was therefore allowed to remain overnight. The next morning it was observed that the mixture had produced a brown precipitate and a green supernatant liquid. Neither the liquid nor the precipitate exhibited the same absorption maxima as the compound of interest and they were therefore discarded. The next attempt at synthesis was more drastic. One gram PDA-bromide was refluxed for two hours with 100 ml 2:1 nitric acid under reduced pressure and low heat. The resulting brown solution was diluted with water whence a bright yellow-orange material separated as a flocculent precipitate. The mixture was neutralized with sodium bicarbonate to ~ pH 5 and filtered. The precipitate was washed several times with water until the fitrate was free from nitrate. Thin layer chromatography of this material yielded only 3 principal spots, and the ultraviolet spectrum of the gross

product in acidic and basic solutions had absorption maxima close to the compound of interest. Therefore, it was decided to separate the mixture into its individual components. Attempts to separate by fractional crystallization failed. Attempts to separate by thick layer chromatography was abandoned because of poor separation of bands even upon repeated development with various solvents. High pressure liquid chromatography would have probably been the choice method to separate the material but available facilities did not permit such an approach. Another problem was that the material thus obtained exhibited very little solubility and therefore to separate any significant quantity, a substantial amount of solution needed to be used. Further, the material was so intensely colored that it was difficult to judge its solubility in different solvents. Even very small amounts dissolved produced such dark solutions that it was impossible to judge how much of it was left undissolved. It was clear however, that the material was more soluble in polar than in non-polar solvents, although ethanol and methanol were not particularly good for the purpose. Acetone, dimethylsulfoxide, and acetonitrile were found to be the best among those tested, and since not a great deal of difference was noted among these three, acetone solutions were used for component separation purposes. In regard to solubility it is interesting to note that although the product solubility in water was poor, the solubility in strong acid was fair and in strong base almost as good as in acetone.

Component separation was achieved finally by column

chromatography on a 75 cm long 4 cm diameter column packed with silica gel - 60; (200 mesh) with a 500 ml solvent reservoir on top. Earlier attempts to separate successfully on a smaller length column failed, as did the trial of activated alumina as a substrate. The latter retained the material so tenaciously that hardly any movement was observed by elution with any of the common solvents.

About 0.5 g of the product was dissolved in 30 ml. warm acetone (saturated solution) and injected at the top of the silica-gel column and then eluted with a mixture of 1:2 cyclo-hexane: Ethylacetate at the rate of about 1 ml/min. As colored material began to elute, 25 ml. aliquots were collected and each portion was analyzed by thin layer chromatography and accordingly mixed. Three main fractions were obtained; each one containing one principal component and impurities. The first eluted fraction was evaporated, redissolved in acetone and separated from impurities by thick layer chromatography and recrystallized from 95% ethanol. Only about 10 mg of the compound (A) was obtained.

The second fraction eluted was evaporated, redissolved in acetone, and purified by column chromatographing a second time. The eluent was evaporated and recrystalized from 95% ethanol. About 150 mg of this compound (B) was obtained. The third fraction was also purified by column chromatography and recrystallized from ethanol. The yield of this compound (C) was about 300 mg.

II. STRUCTURAL ANALYSIS

Since amines of the perimidine family are in general quite susceptible to oxidation (PDA as a free base is rapidly oxidized

by air) it was taken for granted that PDA has undergone some form of oxidation, possibly producing a carboxylic acid or a conjugated nitro carboxylic acid and hence the color. This hypothesis was reinforced by formation of similar colored products by reactions with other oxidizing agents such as chlorine water, etc. (cf., Chapter VII) and the fact that all of these compounds were fairly soluble in strong base and behaved as pH indicators.

Qualitative elemental analysis established the presence of nitrogen in all the three compounds. No bromine was detected in any of the compounds at first, an error that resulted in much lost time. Cyanide was formed during the sodium fusion test in the presence of nitrogen and required removal by boiling with nitric acid before tests for halogens could be carried out. Bromine was later detected in compounds A and B. The reason that it was missed the first time was probably because the bromine was driven off from the test solution as nitrosyl bromide during boiling with nitric acid.

On boiling with zinc dust and ammonium chloride in alcoholic solution all the three compounds were first bleached to a pale yellow color, then rapidly turned dark purple by air oxidation. An aliquot of the freshly reduced solution was filtered into ammoniacal silver nitrate, and silver was precipitated indicating the presence of $-NO_2$ groups. None of the three compounds formed a blue or green color with diphenylamine in sulfuric acid indicating absence of $- ONO_2$, $- ONO$, $=NNO_2$, $=NNO$ and possibly $- NO$. The purple solutions referred to above produced a blue coloration

with diphenylamine reagent thus further confirming the presence of nitro groups in the compounds. Zinc dust and ammonium chloride in ethanol reduces nitro compounds to hydroxylamines which in turn are air oxidized to nitroso compounds,

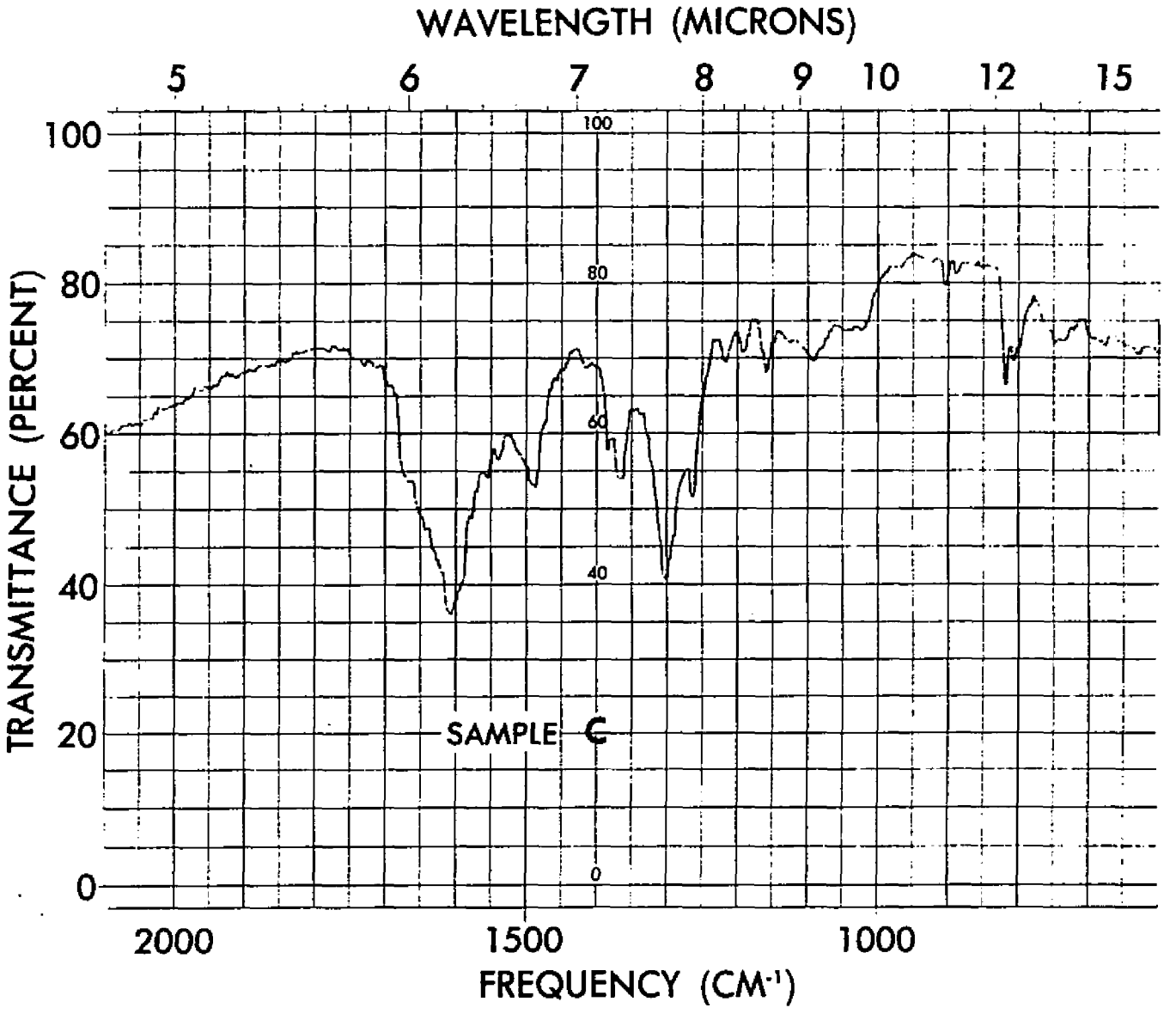
$$-NO_2 \xrightarrow[EtOH]{Zn/NH_4Cl} -NHOH \xrightarrow{Air} -NO$$

Nitroso compounds, unlike nitro compounds, oxidize diphenylamine.

Infrared spectroscopy further substantiated the presence of nitro groups; the strongest absorption band in all the three compounds was observed around 1600 cm^{-1}. In addition an absorption band at 980 cm^{-1} was present in compounds A and B and was attributed to aromatic carbon-bromine stretch. A representative spectrum, that of compound C is shown in Figure 10. Strong broad band absorption was present in all the three compounds around 3500 cm^{-1}, but since occlusion of moisture in potassium bromide pellets was unavoidable, no positive conclusions could be made regarding the presence of - OH and/or > NH groups. No > C=O stretch was present and thus the possibility of the compounds being carboxylic acids was ruled out.

Mass spectra definitely established the presence of one bromine atom each in compounds A and B, in each case yielding two parent peaks at mass numbers 396 and 398 of equal intensity. Two parent peaks separated by one mass unit and of equal intensity is a characteristic of compounds containing one bromine atom since the abundance ratio of the two bromine isotopes 79 and 81 is

FIGURE 10


WAVELENGTH (MICRONS)
5
6
7
8
9
10
12
15
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
SAMPLE C
2000
1500
1000
FREQUENCY (CM-1)

almost unity. In contrast, no bromine was present in compound C and the parent mass number was 363. (Figure 11)

With the help of elemental analysis data and the molecular weight from mass spectra (substantiated by osometric molecular weight measurements) the following molecular formulas were established.

A and B: $C_{11}H_5N_6O_6Br$

C: $C_{11}H_5N_7O_8$

A and B therefore appeared to be a pair of structural isomers. From the number of carbon and nitrogen atoms it was suspected that actually no oxidation had taken place and the whole PDA nucleus was completely intact. Proton magnetic resonance (PMR) spectra (Figure 12) showed only a single peak at 0.68τ for compound C and the spectra of compounds A and B were virtually identical, each yielding two separate singlets at $\sim 0.79\tau$ and $\sim 0.98\tau$.

In all cases signals due to the protons on the nitrogen atoms were also present ($1.07 - 1.27\tau$). This resonance was very broad due to interaction with the solvent and could be readily identified since an identical resonance was exhibited by the protons on the nitrogen atoms in PDA-bromide. All evidence therefore indicated compound C to be 2-amino 4,6,7,9-tetranitro-perimidine (Structure I, Figure 13).

It must be realized that in PDA the doubly bonded and the singly bonded ring nitrogens can easily change their identities through an acid catalyzed proton shift. At ordinary temperatures,

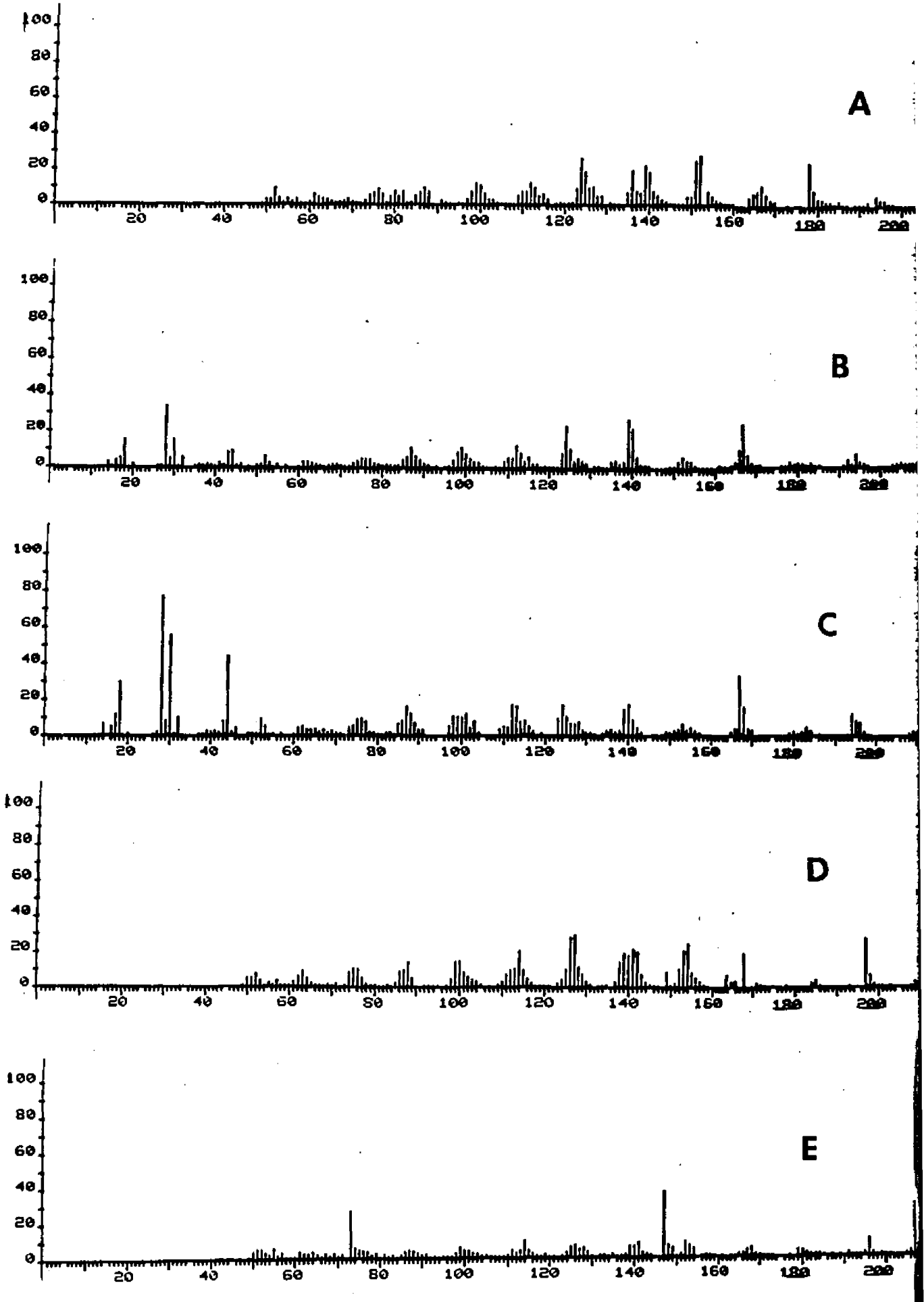
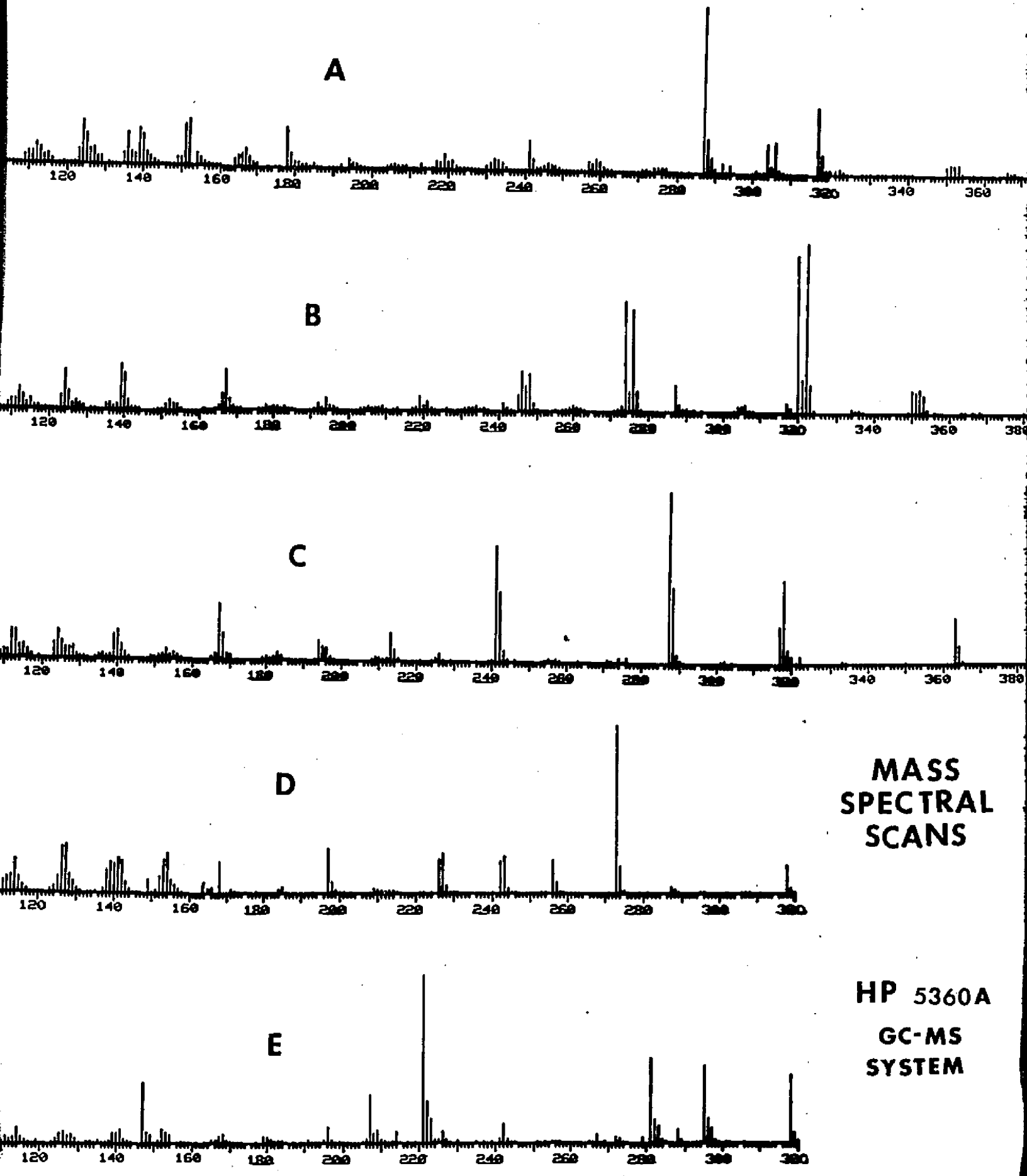


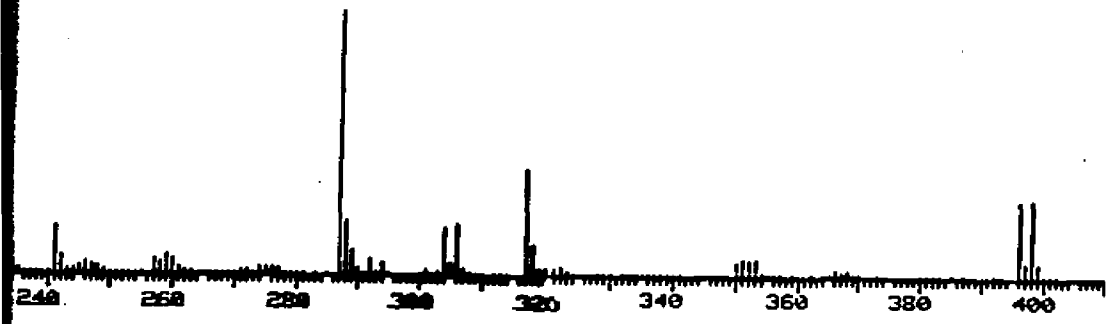
FIGURE 11

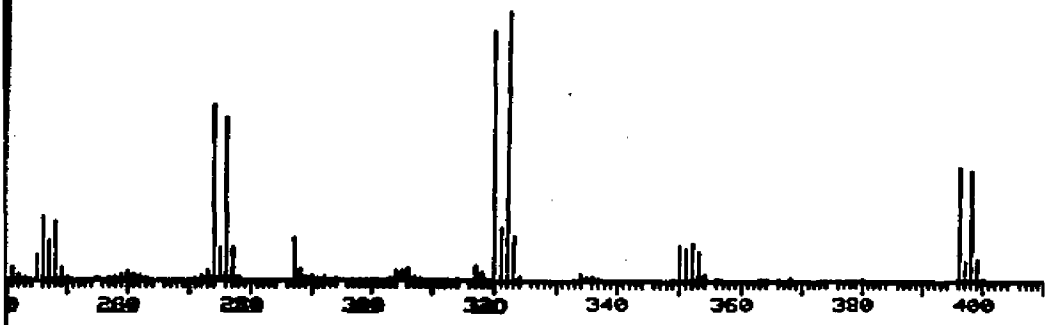


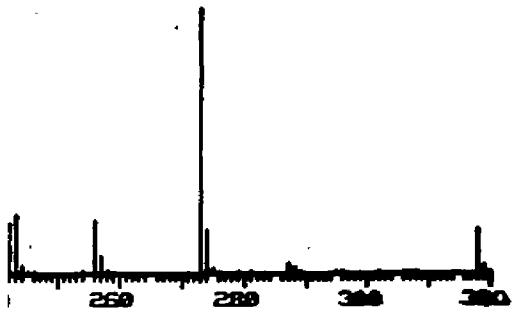
MASS SPECTRAL SCANS

HP 5360A

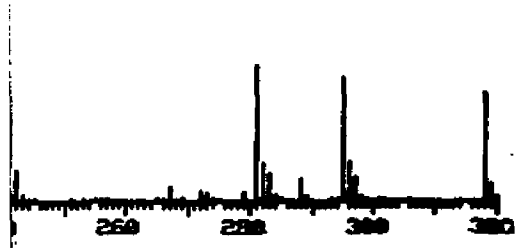
GC-MS SYSTEM







MASS SPECTRAL SCANS



HP 5360A GC-MS SYSTEM

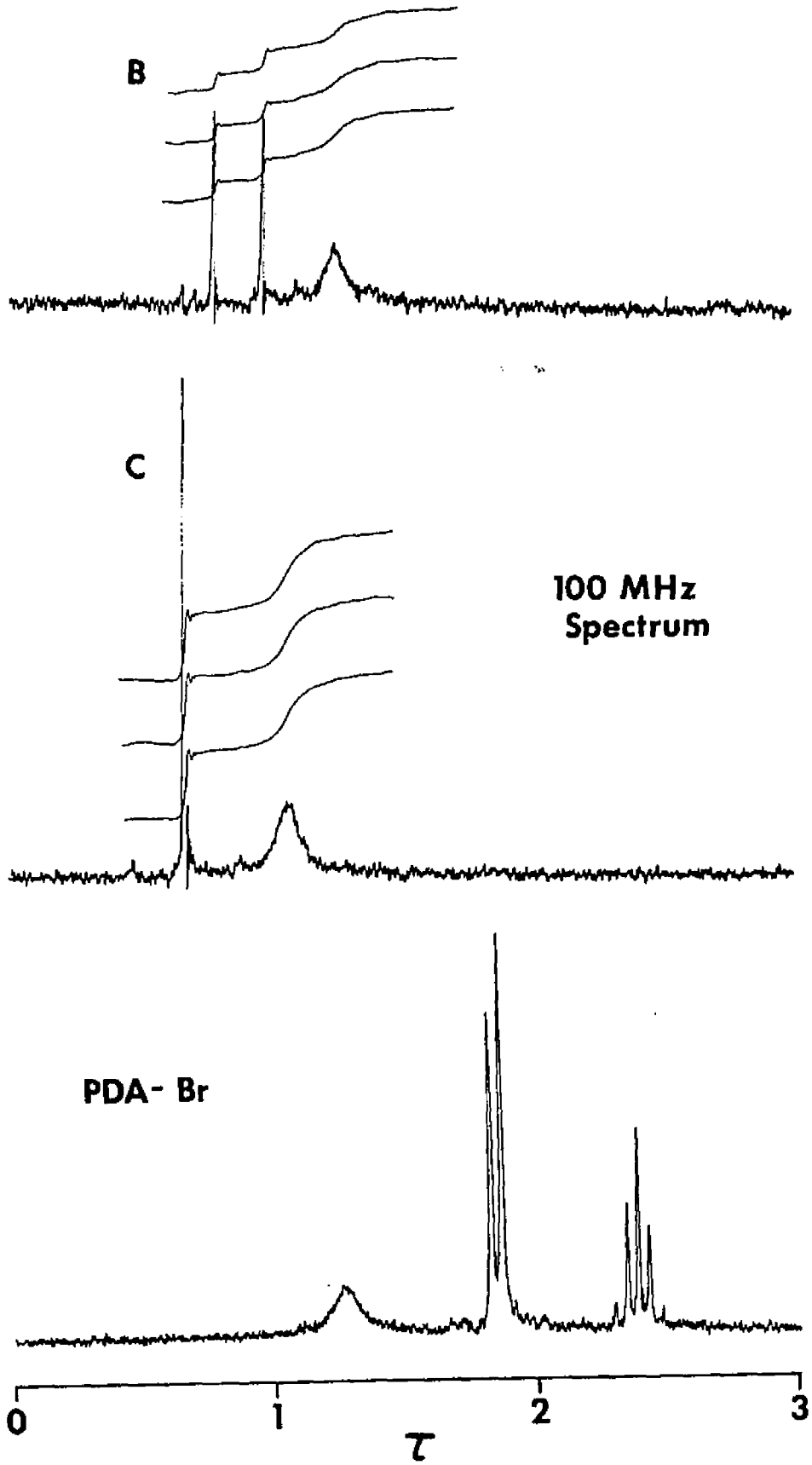
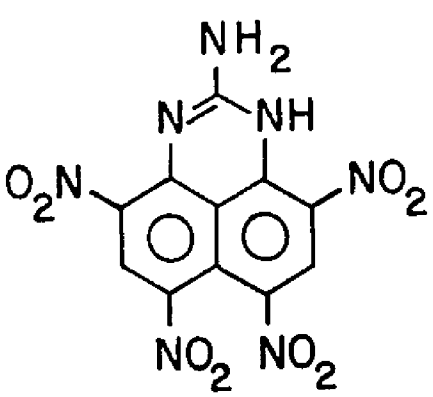
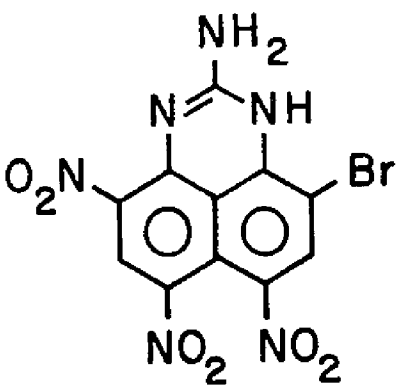


FIGURE 12

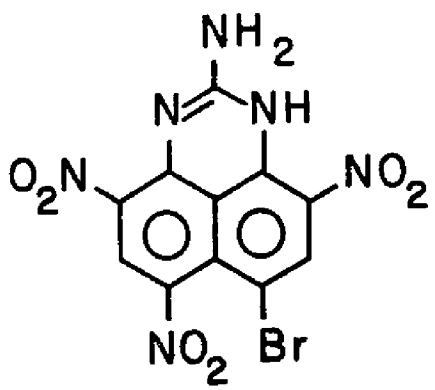
FIGURE 13



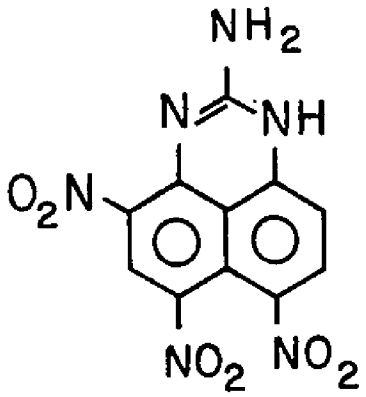
I



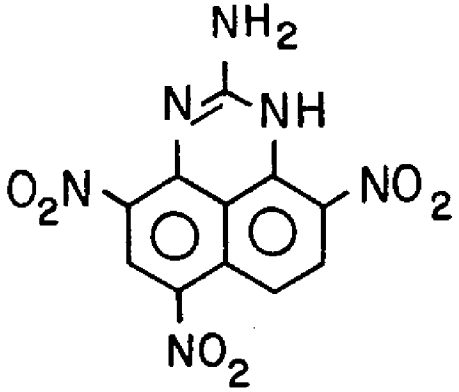
II



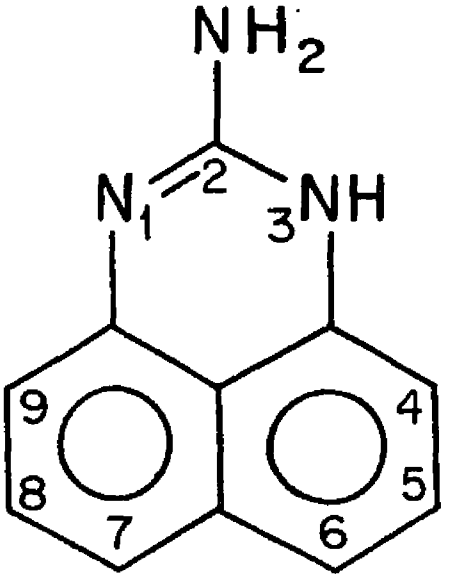
III



IV



V



this exchange is expected to be relatively fast, such that no differentiation between the two forms in a ring substituted PDA-derivative is expected to be discernible by nuclear magnetic resonance spectroscopy. Even if this interchange could be made slower by lowering the temperature (decreased sample solubility ruled out experimentation), it is doubtful that there would have been a significant difference in chemical shifts of the proton pairs at positions 4 and 9, 5 and 8, and 6 and 7 respectively. In other words, for all practical purposes the substitution sites 4, 5 and 6 are chemically identical to those at 7, 8 and 9 respectively. From a mechanistic viewpoint, the electromeric effects of the ring nitrogens and the meta directing tendencies of a nitro group once introduced into the ring makes the substitution at the positions 4, 6, 7 and 9 the only logical choice for the four nitro groups. This was further confirmed by the symmetrical substitution as evidenced by the ^{13}CMR spectrum,

as well as the position of the signal in the PMR spectrum. The resonance at 0.68τ was indicative of a very acidic hydrogen, flanked by two nitro-substituted carbons, rather than its being adjacent to only one. (The PMR signal for s-trinitro benzene is located at 0.88τ; in m-dinitrobenzene the signal for the flanked hydrogen is at 0.99τ while the hydrogens adjacent to only one nitro group resonate at 1.41τ).[431] The hydrogens in this compound were in fact unusually acidic for ring protons, the NMR signal instantly vanished upon D_2O addition.

Very obviously therefore, A and B were the two possible monobromo trinitro derivatives (Structures II and III). As has been mentioned before, positions 4 and 9, and 6 and 7 were respectively identical and therefore there were only two possible isomers, the bromine in one case being ortho to the heterocyclic ring (II) and in the other case para to it (III). Now the problem was to ascertain which compound corresponds to which structure, a problem that was by no means trivial because conventional structural tools (NMR, IR, etc.) are unable to unequivocally differentiate between the two. The only available structural tools that could have solved the problem was X-ray diffraction or electron microscopy. In either case however, a perfect single crystal of reasonable size was required, and this proved to be impossible to obtain.

A rather novel approach was taken, stimulated by this author's prior experience[465] of electrochemical work with a number of dinitroaniline compounds. From polarographic evidence

Structure III was assigned to Compound A and Structure II to Compound B. To the best of this author's knowledge, polarographic data have never actually been applied to the elucidation of structure.

Aromatic nitro compounds belong to a class that has been subject to extensive electrochemical investigation in the past,[209] possibly because of its ease of electrochemical reduction to hydroxylamines. The nitro group is reduced to a hydroxylamine in a direct 4 electron step.

$$- NO_2 + 4H^+ + 4e \longrightarrow - NHOH + H_2O$$

It was obvious from the equation that availability of hydrogen ions, i.e., the pH would govern how easily the reduction can proceed, i.e., where the polarographic half wave reduction potential would be located. Indeed, pH greatly affects the half wave potential. In going from strongly acidic to strongly basic solution the potential shifts towards more negative values and the difference may be as high as 1500 millivolts.

Reduction of the hydroxylamine group all the way to the amino group by a 2-electron step reduction

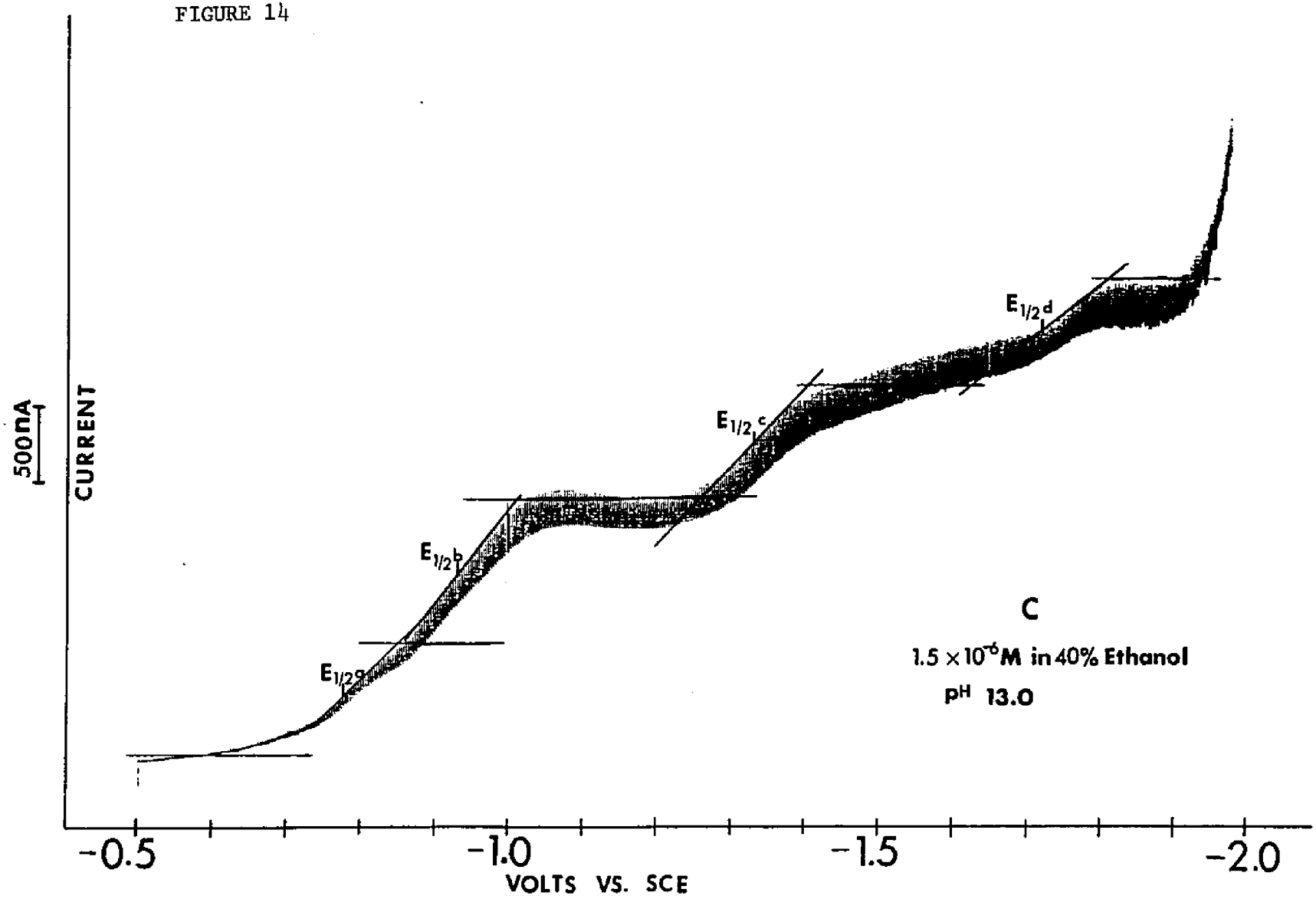
$$- NHOH + 2H^+ + 2e \longrightarrow - NH_2 + H_2O$$

is difficult and according to the studies on dinitroaniline compounds of Southwick et al.[464] this reduction does not normally take place. Actually this reduction step was only feasible in strongly acidic media, presumably due to the formation of the

$-NH_3^+$ group and thus favoring the equilibrium shift and lowering of the reduction half wave potential. Otherwise, this reduction would be so difficult that the solvent medium itself would begin to decompose before the necessary reduction potential could be reached. The problem was not however, all that straighforward because solvent breakdown itself is also a function of pH. In 40% ethanol, for example, the usable range at pH 1.5 is at best up to -1.0 volts (vs. the S.C.E.) while at pH 13.0 solvent breakdown does not occur until $\sim$ -1.9 volts. The salient point is that, in general, we can disregard the possibility of reduction to amino groups.

For a compound containing more than one nitro group the reductions proceed in stages, except at low pH, in the latter case reduction steps are far too facile to permit separation. Excellent separations are achieved at high pH values, four distinct reduction waves can be observed in the polarogram of the tetranitro compound at pH 13.0 before the solvent breaks down (Figure 14). The ratio of wave heights in this particular polarogram was 0.97:1.2:0.92:0.92 confirming that we were observing the stepwise reduction of four nitro groups to four hydroxylamino groups. The wave height or more strictly the respective diffusion currents each correspond to a four electron reduction step. Theoretically, one could argue that the diffusion currents should all be identical, but the diffusion current is not only directly related to the number of electrons involved in the reduction step but also to the diffusion coefficient of the particular

FIGURE 14


500nA
CURRENT
$E_{1/2}{}^{a}$
$E_{1/2}{}^{b}$
$E_{1/2}{}^{c}$
$E_{1/2}{}^{d}$
C
1.5×10^{-6}M in 40% Ethanol
pH 13.0
-0.5
-1.0
-1.5
-2.0
VOLTS VS. SCE

species involved. Starting with the tetranitro compound, the second wave was due to the reduction of the trinitromonohydroxylamino species, the third wave was due to the reduction of the dinitrodihydroxylamino species and so on.

There is no reason to believe that these species will all have absolutely identical diffusion coefficients. From a standpoint of size, which is the dominant factor governing diffusivities, it may be expected that the diffusion coefficients of the four species involved should be fairly close to each other. However, chemical interaction of these species with the medium also controls diffusivities to a certain extent and since the chemical nature of the species changes as the reduction progresses, a strict assessment of diffusion coefficients could not be made. In addition, the physical characteristics of a mercury drop do not remain identical at various applied voltages and because of various real life factors such as incomplete separation and varying background current, polarographic maxima at lower voltages that can never be completely eliminated by maxima suppressors (note the bulge on top of the second wave), slopes at the higher end due to the onset of medium breakdown, estimation of diffusion currents due to each step are never one hundred percent accurate. However, there is no doubt that a -NHOH to $-NH_2$ reduction step in this polarogram (or others not shown) is absent. If such a reduction occurred a wave with approximately half the height of the first reduction step ($-NO_2$ to -NHOH) would have been observed since only two electrons are involved in such a step as opposed

to four.

We have not so far assigned which nitro groups are reduced in what order, and such assignments are only possible with the help of studies on model compounds. PDA itself may be considered to be derived from 1,8-diamino naphthalene (this compound in fact is used for the synthesis of PDA-bromide which in turn can be thought to be two aniline rings fused together. Nitro-substituted anilines therefore can be used as reasonable models for nitro-substituted PDA compounds.

Fortunately such studies were available in the literature.[209] Exactly a quarter century ago Holleck and Exner[208] reported a thorough investigation of nitro substituted anilines. From the study of o-nitroaniline, p-nitroaniline and o,p-dinitroaniline, they concluded that the two reduction steps are well separated for the last compound and the o-nitro group is reduced first. In fact, this group is reduced somewhat more easily (i.e. at a less negative potential) than the nitro group in o-nitroaniline due to the effects of the second nitro group. The nitro group in the para position is reduced more difficultly (i.e., at a higher negative potential) than the nitro group in p-nitroaniline because of the formation of the hydroxylamine group in the o-position, prior to the reduction of the nitro group in p-position. The half wave reduction potentials were well separated ($\sim$ 250 mv) even at the pH of 3.1. With this information at hand it was possible to assign the observed polarographic waves to specific nitro gropus. In addition, it should be pointed out at this stage that reduction

does not necessarily begin simultaneously for two nitro groups in chemically identical positions. A model example is that of m-dinitrobenzene, studied first by Pearson[379] and later by Southwick, et al.[465] One of the nitro groups was first reduced, producing a hydroxylamine which made the reduction of the second nitro group more difficult and therefore a separation was observed; although to start out with the two nitro groups were identical.

Polarographic data are summarized in Table XII. All experiments were carried out in 40% alcoholic solution. The solution concentration was $\sim 1.5 \times 10^{-6}$M in each case. Sodium chloride was used as the supporting electrolyte, Triton-X-100 as maxima suppressor, and otherwise the general set-up was the same as described by Southwick, et al.[465] The table lists the observed half wave potentials and the ratio of the corresponding wave heights in parentheses. The later data was in fact the more important clue to the problem since at all but extremely high pH values complete separation was impossible and more than one group was reduced in what appeared to be a single step. The wave height of course, immediately revealed how many groups were involved in a given reduction step. All calculations were made by measuring the diffusion current at the top of the recorder oscillation trace as is customary for irreversible reductions.

If we look at the data for the tetranitro compound at pH 13.0, the first wave must be due to one of the o-nitro groups since as has been mentioned they were reduced preferentially to the p-nitro groups. The second wave must be due to the other o-nitro

TABLE XII

POLAROGRAPHIC DATA

pH	HALFWAVE REDUCTION POTENTIALS (In Negative millivolts vs. SCE) Ratio of Corresponding Waveheights in Parentheses			
	First	Second	Third	Fourth
	Compound A (Trinitro monobormo -)			
2.1	115 (1.8)	260 (1)		
4.5	155 (1.0)	335 (1.0)	480 (.98)	
7.2	318 (.92)	448 (1.0)	655 (1)	
9.0	490 (1.0)	608 (.92)	966 (.91)	
	Compound B (Trinitro monobromo -)			
9.0	484 (1.0)	973 (2.1)		
13.0	790 (1.0)	1205 (.94)	1560 (1.2)	
	Compound C (Tetranitro -)			
2.1	115 (2.0)	255 (2.1)		
7.2	315 (.92)	435 (1.1)	634 (2.0)	
9.0	420 (.92)	525 (1.2)	894 (2.0)	
13.0	775 (.97)	930 (1.2)	1330 (.92)	1720 (.92)
	Compound D (Trinitro -)			
9.0	510 (.98)	980 (2.0)		
13.0	820 (1.0)	998 (1.1)	1392 (.93)	
	Compound E (Trinitro -)			
9.0	502 (0.980	660 (1.1)	950 (1.0)	
13.0	814 (1.0)	1302 (.90)	1580 (1.0)	

* 1.5×10^{-6}M solutions in 40% Ethanol

All ratios calculated with 800 nA = unity

group since the separation between the first two half wave potentials was only 155 mv apart and if the second one was due to a p-nitro group it would have been further apart. The third and fourth waves were then due to the two p-nitro groups. Going down in pH the first thing that happened was that the last two steps occurred together and could not be separated.

At the next lower pH this was still the case and finally at a pH of two the o-nitro groups underwent reduction in one step and the two p-nitro groups in one step. In the trinitromonobromo compounds the presence of a bromine instead of a nitro increased the ring electron density somewhat and reduction was expected to be more difficult. This is what was observed and for compound A at pH 9.0 the first, second and third half wave potentials were somewhat higher compared to the corresponding data for the compound C. The wave height ratio in this case was roughly 1:1:1 as opposed to the 1:1:2 ratio observed in C. The data clearly pointed out that if the reduction order for compound C was ortho, ortho and two para's, then that observed for compound A must have been ortho, ortho and para. The second para nitro group was missing and therefore the bromine must have been in the para position. Therefore, Structure III was assigned to A; the data for A at other pH values merely confirmed this.

With B it was observed that the first half wave potential at pH 13.0 was slightly higher than the corresponding value for the tetranitro compound as expected because of increased ring electron density. There were, however, no waves corresponding to the

second wave of the tetranitro compound at pH 13.0 ($E_{1/2}$ 930 mv). The second wave observed for Compound B ($E_{1/2}$ 1205 mv) was too far removed in location from that of C to be the corresponding wave. It must therefore, correspond to the third wave of C. The reason that it was located at a potential lower and not higher than that of C was because by the time the third step of the polarographic reduction of C began two hydroxylamino groups had been introduced in place of two nitro groups which significantly increased the ring electron density, while by contrast only one hydroxylamino group was present in the case of B at this time. The third wave of B therefore corresponded to the fourth wave of C and was located at somewhat more positive values because of the above reason. The net result was that the second o-nitro group that gave rise to the second wave in C was not present in B. The bromine therefore must have been in the o-position in the compound and Structure II was assigned to B. The data at pH 9.0 supports this conclusion.

It was obvious of course, that the reaction product of our analytical interest could not be compounds A or B. Further examination of C revealed somewhat different absorption characteristics in the uv-visible spectra from the material formed on the filter. Therefore, the problem of establishing the identity of the product of the analytical reaction remained still unsolved and efforts to this end had to be restarted.

III. SYNTHESIS: Five hundred milligrams of PDA-sulfate was suspended in 25 ml methanol by ultrasonic agitation and 25 ml of

concentrated nitric acid added. After allowing it to react for 5 minutes the mixture was diluted with water, neutralized with sodium bicarbonate and filtered. The precipitate was washed with water until free from nitrate. Thin layer chromatography showed the presence of only two principal components and one present in much larger excess than the other. Separation of the mixture by column chromatography proved exceedingly difficult, apparently the two compounds had very similar properties. Elution was accomplished with 2:1 cyclohexane:ethyl acetate and the fractions had to be chromatographed 4 times, taking a total of more than 60 hours before each component could be obtained in pure form. Only 25 mg of the faster eluting component (compound D) and about 100 mg of the other compound (E) was obtained in pure recrystallized form.

IV. STRUCTURAL ANALYSIS: Prior experience with the first three compounds made the structural analysis of these two compounds fairly easy. Elemental analysis indicated only C, H, N, O and no sulfur, (also, during synthesis, sulfate ion was detected in the solution after filtering off the product). Mass spectral scan showed the same parent mass of 318 (Figure 11) for both compounds; and both compounds also had the same elemental composition indicating a pair of structural isomers with the molecular formula $C_{11}H_6N_6O_6$. Obviously these were the two possible trinitro derivatives. Again, by polarography structure IV was assigned to Compound D and Structure V to E. Table XII lists the data and corresponding values are higher for D and E than with C, because

of increased ring electron density due to the absence of one nitro group. In this case, however, it was possible to substantiate the polarographic conclusions by PMR spectra.

Further, study of the pH-dependent visible absorption spectra of E matched exactly with that of the product obtained in the analytical reaction, establishing the identity of the latter. The R_f values on thin layer plate was also found to be identical.

Assigned structures together with theoretical and found elemental percentages of the various compounds are listed in Table XIII. A search of chemical formula-name indices revealed that none of these compounds have ever been reported. This is, of course, not surprising in view of the fact that our knowledge of the chemistry of perrimidines is quite limited.

V. SOME PROPERTIES OF NITRO SUBSTITUTED 2-AMINO PERIMIDINES

A. VISIBLE ABSORPTION

All of the compounds were highly colored, varying in hue in the solid state between yellow and dark red. The compounds were isolated in a microcrystalline state. A microphotograph of the tetranitro compound is shown in Figure 15. The magnification on the photograph is 500X. The crystal apparently belongs to the C_{2v} symmetry class and as such did not contradict the assigned structure. In solution, all the five compounds behaved as pH indicators, the color in strongly acid solutions being yellowish green and changing through yellow and various shades of orange (for the different compounds) as the pH was increased, coming finally to orange or deep purple in strongly basic solutions. It

TABLE XIII

RESULTS OF ELEMENTAL ANALYSES

COMPOUND	STRUCTURE	MOLECULAR FORMULA	COMPOSITION % C T	% C F	% H T	% H F	% N T	% N F	% O T	% O F	% Br T	% Br F
A	III	$C_{11}H_5N_6O_6Br$	33.27	32.91	1.27	1.25	21.16	20.91	24.17	24.22	20.12	19.86
B	II	$C_{11}H_5N_6O_6Br$	33.27	33.11	1.27	1.25	21.16	20.96	24.17	24.49	20.12	21.01
C	I	$C_{11}H_5N_7O_8$	36.37	35.86	1.39	1.37	26.99	26.1	35.29	36.01		
D	IV	$C_{11}H_6N_6O_6$	41.52	42.01	1.90	1.86	26.41	25.20	30.17	31.52		
E	V	$C_{11}H_6N_6O_6$	41.52	42.32	1.90	1.82	26.41	26.10	30.17	31.02		

T: Theoretical

F: Found

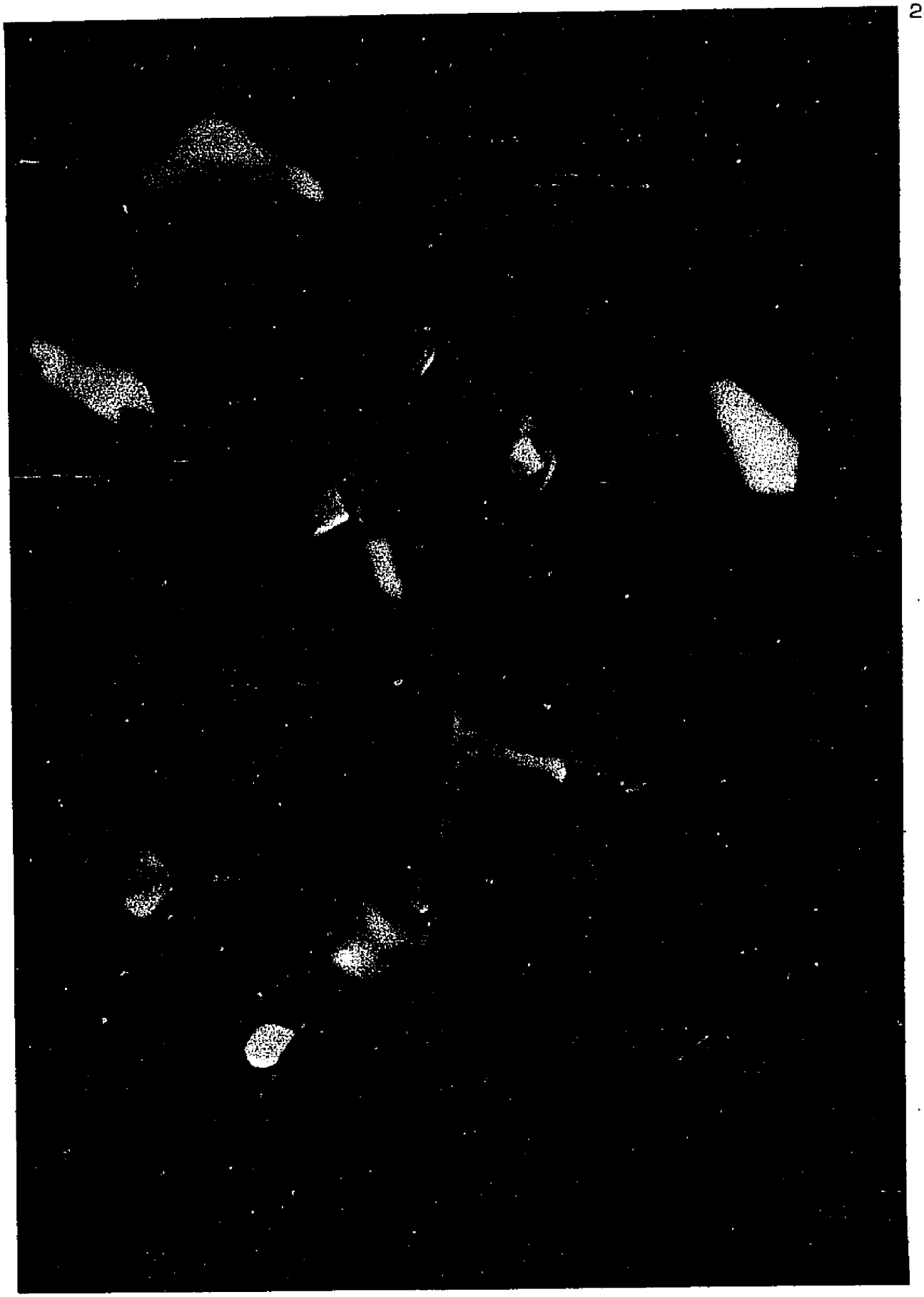


FIGURE 15

was reasonable to assume that three different species were involved: the neutral compound, the monoprotonated species, the amino group at 2-position being protonated and the diprotonated species, the ring amino nitrogen being also protonated. A thorough study was undertaken to study the variation of the visible spectra of the five compounds with pH. The tetranitro compound being chemically the most interesting was studied at every 0.2 pH unit from 0.0 through 9.0 and the others were studied at every integer pH unit from 0.0 through 9.0. These studies also showed that beyond a pH of $\sim$ 10, there was no further change in spectral characteristics for any of the compounds. These studies were done in all but the first case with a computer interfaced spectrophotometer so that the task of the data processing and plotting was manageable. The wavelength range studied was 350 - 600 nm. Figure 16 shows a 3-dimensional (wavelength, pH and absorbance) plot of the tetranitro compound and Figure 17 depicts a family of absorbance vs. wavelength curves at different pH values for the same. The first set was from pH 0.2 to 2.0 at every 0.2 pH unit and the second set was from pH 0 through 9 at every integer pH unit. The occurrence of three separate isosbestic points at the wavelengths 388 nm, 478 nm and 426 nm could be easily perceived. The first two isosbestic points both were due to the equilibrium between the neutral and monoprotonated species and the last one was due to the equilibrium between the diprotonated and the monoprotonated species. Three such isobestic points existed for all the other compounds

FIGURE 16

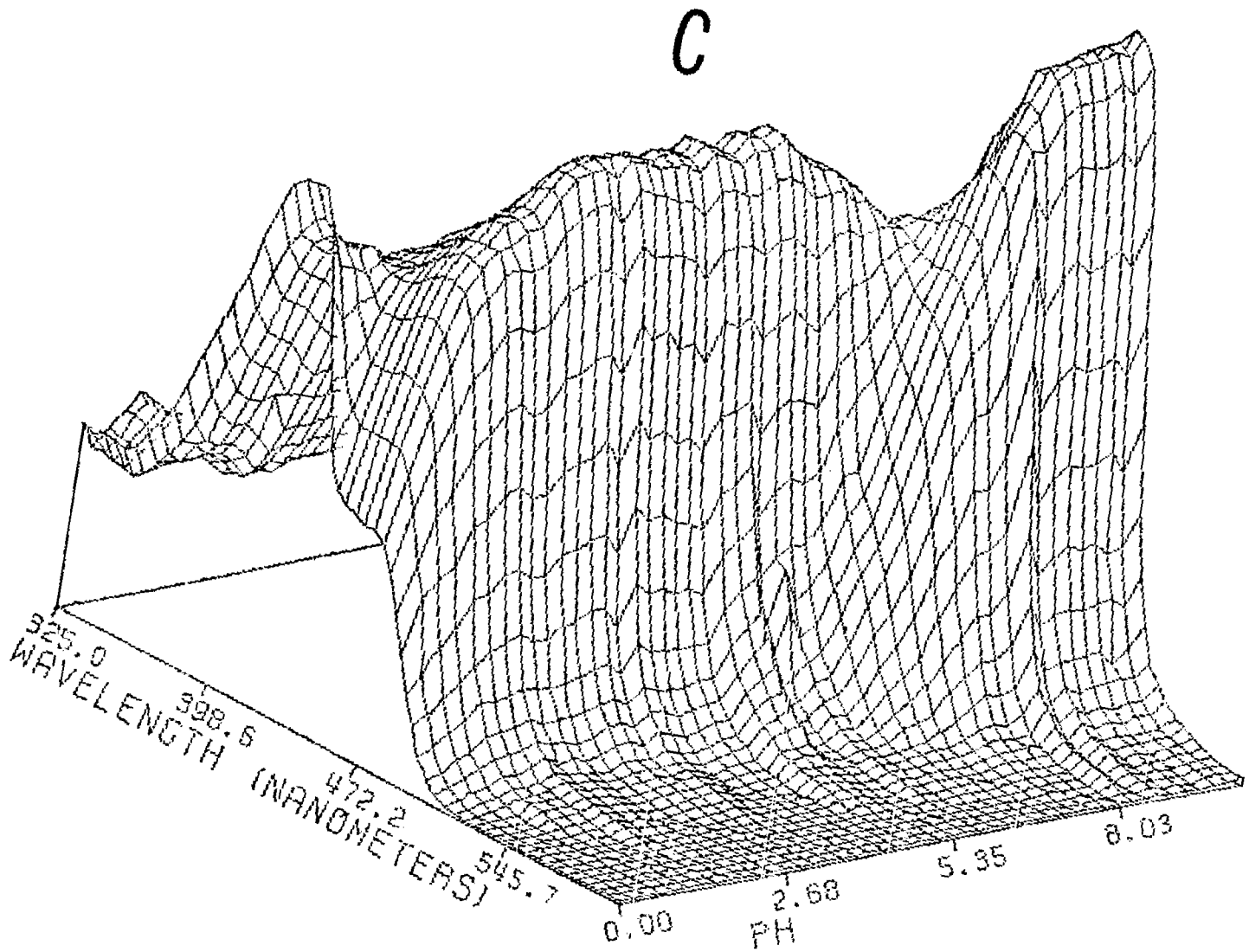
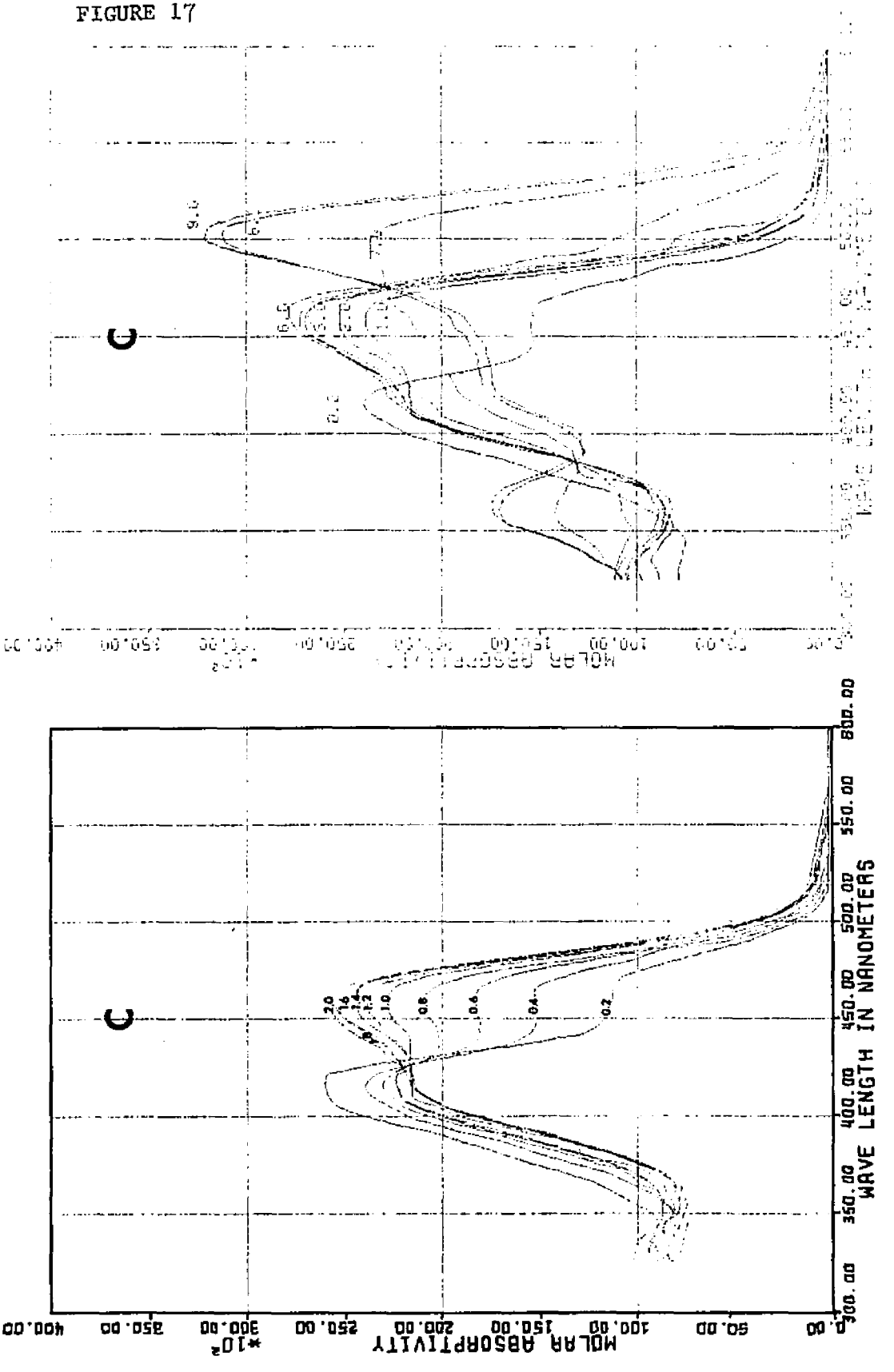

C
325.0
398.6
472.2
545.7
WAVELENGTH (NANOMETERS)
0.00
2.68
5.35
8.03
PH

FIGURE 17


MOLAR ABSORPTIVITY
*10²
WAVE LENGTH IN NANOMETERS
C
2.0
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2

as well. The plot on the left in Figure 18 again for Compound C, shows the absorbance vs. pH plots for a family of curves at different wavelengths (with the wavelength in nm marked on each curve) and the plot on the right shows the molar absorptivity contour map of the pH and wavelength plane. Figure 19 shows the 3-dimensional plots for all the other compounds. The three dimensional data matrix for each compound was handled by two computer programs WESTSAS and WESTSAS2 developed especially for this purpose based on the statistical analysis system (SAS) software developed by Barr, Goodnight, Sall and Helwig.[436] The programs provided the equilibrium constants K_2 and K_1 for the reactions $H_2D^{2+} \rightleftharpoons HD^+ + H^+$ and $HD^+ \rightleftharpoons H^+ + D$ respectively where D is the neutral compound and evaluated the best values after a non-linear least squares search. A brief description of the programs and their mathematical basis is given in appendix III. A summary of information obtained from spectral study is listed in Table XIV. Correlation coefficients for the pK values (pK = -log K) were better than 0.97 in all cases.

B. THERMAL DECOMPOSITION

The thermal decomposition characteristics of highly nitro substituted aromatic compounds are always interesting and all the five compounds were therefore thoroughly studied thermogravimetrically and by differential scanning calorimetry (DSC). The nitrogen used for purging was freed from oxygen by passing over heated copper at 300°C, without such removal of oxygen erratic results were obtained. For DSC runs the samples were put in

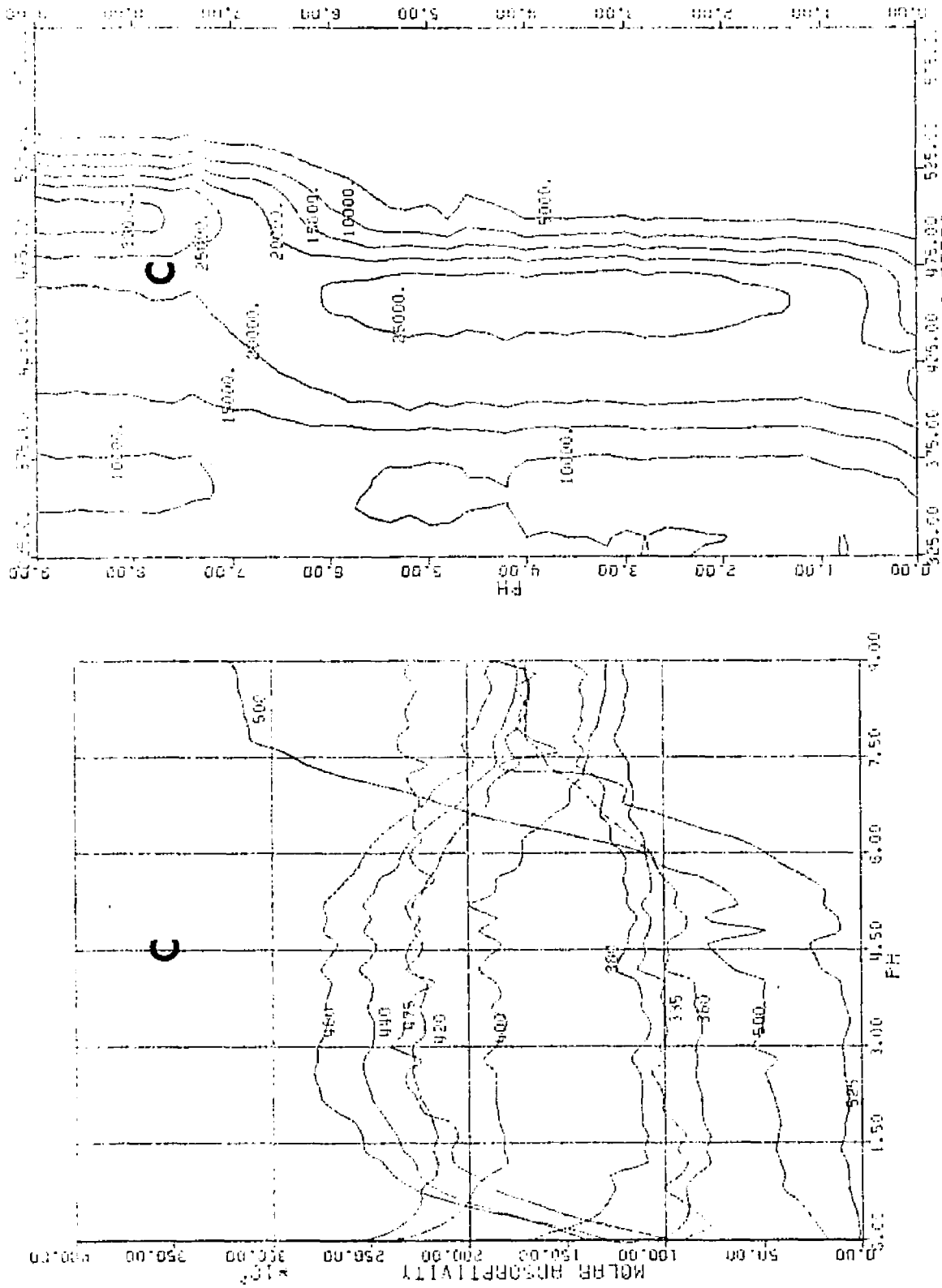


FIGURE 18

FIGURE 19

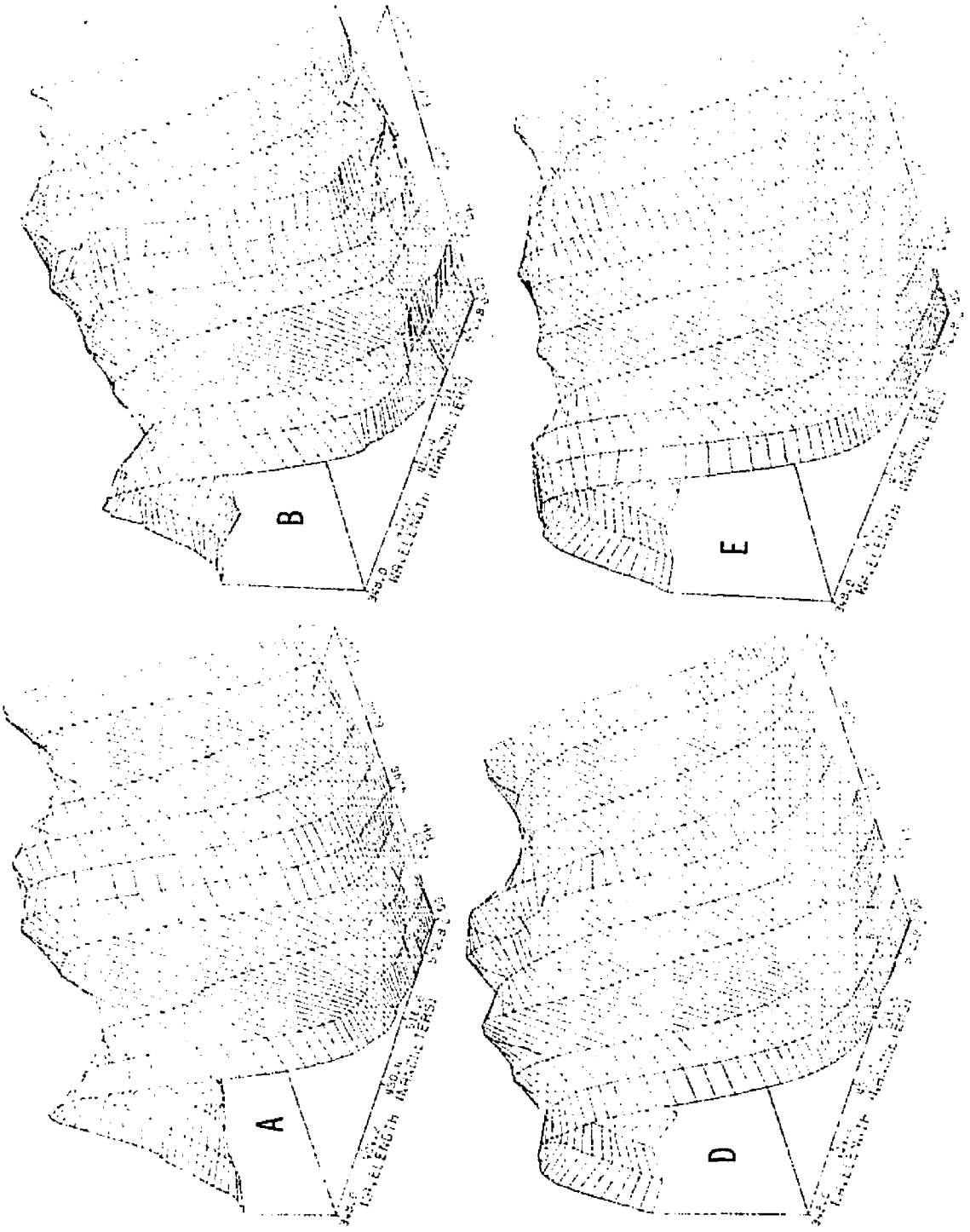


TABLE XIV

PROPERTIES OF NITRO SUBSTITUTED 2-AMINO PERIMIDINES
AS CALCULATED FROM SPECTRAL DATA

COMPOUND	STRUCTURE	ACID DISSOCIATION CONSTANTS pk_2	ACID DISSOCIATION CONSTANTS pk_1	ABSORPTION MAXIMA OF NEUTRAL SPECIES (High pH Runs) nm Rounded to Nearest 5 nm	MOLAR ABSORPTIVITY AT ABSORPTION MAXIMA x 10^4
A	III	2.72	6.92	530	1.70
B	II	2.44	6.62	510	1.80
C	I	2.92	7.10	500	3.11
D	IV	2.40	6.52	485	1.30
E	V	2.64	6.80	550	1.35

hermetically sealed capsules. The heat of decomposition was calculated from the equation

$$\Delta H(\text{mcal/mg}) = E. \frac{\Delta T_S . A. T_S}{M. a}$$

where E = calibration coefficient (mcal.^{o}c/min.) determined at various temperatures with various standard materials according to manufacturer's instructions.[135]

A = Peak area in sq. in., determined by Manual Planimetry

ΔT_S = Y-axis sensitivity in ^{o}c/in.

T_S = X Axis sensitivity in ^{o}c/in.

M = sample mass, mg.

a = heating rate ^{o}c/min.

The results of the thermal investigation are shown in Table XV. All the compounds underwent a flash loss in weight at the decomposition temperature but the exact percent weight loss should be taken as an approximate value because it is quite likely that small amounts were thrown off the boat when decomposition occurred.

In terms of heat liberated, it is unlikely that any of these compounds have any significantly useful explosive properties.

C. FEAGMENTATION PATTERNS IN MASS SPECTRA

It is interesting to note that the mass spectral fragmentation patterns were quite different for the different compounds, especially among the structural isomers (Figure 11). The major peak in the tetranitro compound (C) was located at 287 indicating a loss of 76 mass units from the parent peak. The logical choice to account for this loss was through the loss of one nitro group,

TABLE XV

THERMAL PROPERTIES OF NITRO SUBSTITUTED 2 – AMINO PERIMIDINES

COMPOUND	STRUCTURE	Decomposition Temperature* °C	% Weight Loss During Decomposition	E Calibration Constant at Decomposition Temperature mcal/mg	-ΔH mcal/mg	-ΔH Kcals/mole
A	III	283	40	137	256	101
B	II	307	42	143	259	103
C	I	319	53	146	470	171
D	IV	287	48	139	280	89.0
E	V	307	45	143	276	87.8

* Corrected for thermo couple error

All runs: heating rate 10°C (min., Y-axis sensitivity 0.2°C/in., X-axis sensitivity 50°C/in.

the two ring hydrogens and the top carbon and the amino group; 46+2+12+16 = 76. The same pattern was observed for compound B, the pair of parent peaks were 76 units removed from the pair of major peaks. That the bromine had not been removed at this stage was clear from the appearance of 'paired peaks' at lower mass ranges. In contrast the fragmentation pattern of A showed that the major peak was at 287, respectively 79 and 81 mass units apart from the pair of parent peaks at 396 and 398 clearly indicated a loss of bromine. Compound D had its major peak at 273, 45 mass units from the parent peak, the only feasible way seemed to be due to the loss of the H_2N-C-NH-Link as well as the two ring hydrogens (16+12+15+2 = 45). The spectrum of Compound E appeared to be too complicated to be readily interpreted.

VI. REMARKS

1. Structural assignments were further confirmed by additional synthesis procedures and identification by thin layer chromatography. On boiling with potassium bromide in alcohol compound C was partially converted to a mixture of A and B, principally B. On boiling A or B with sodium nitrate in alchol some conversion to C was observed. D and E both yielded C on boiling with 1:1 nitric acid. The tetranitro compound C was also synthesized later in virtually pure uield by boiling PDA-nitrate with 2:1 nitric acid.

2. Apparently the nitration of the aromatic nucleus takes place in well defined steps. When nitric acid was added to a PDA salt, the mixture went through a green color (which persists only

briefly) which could have been a less nitrated derivative. Attempts were made to isolate this compound by reacting PDA-nitrate with concentrated sulfuric acid, but failed.

PART III

DISCUSSIONS

"Good reasons must, of force, give place to better."

- Shakespeare, Julius Caesar

A. The PDA Cation as a Sulfate Precipitant

To evaluate the superiority of the PDA cation as a sulfate precipitant, the solubility of PDA-sulfate was studied at different temperatures both in water and methanol. The spectrophotometric nitration method was used to calculate the solubility. The results are shown in Figurew 20 and 21, respectively. The only reliable data on the solubility of PDA-sulfate reported is that due to Stephen[469] and it correlates well with this study. Interestingly enough, the solubility curve in methanol shows a minima around room temperature.

With a solubility of only 22 mg/l at 25°C PDA-sulfate is second only to barium sulfate (2.5 mg/l) in insolubility. Although it appears at first sight that this would lead to sensitivity limits an order of magnitude lower, the case is quite different. The solubility product of barium sulfate is 1.08×10^{-10} and that of PDA-sulfate can be readily calculated to be 4.3×10^{-13}. One may of course, wonder how well ionized PDA salts are for solubility product calculations to be applicable. The molecular weight of PDA-bromide was determined by vapor phase osmometry in both water and methanol, in 1% solutions. The apparent molecular weight in water was exactly half of the actual molecular weight and that in methanol was the same as the true molecular weight. In water, therefore, from the observed Vant' Hoff i factor of two, one would conclude that PDA-bromide is completely ionized in water. Following the same argument it is probably not ionized in methanol. The possibility is of course there that in a solution

FIGURE 20

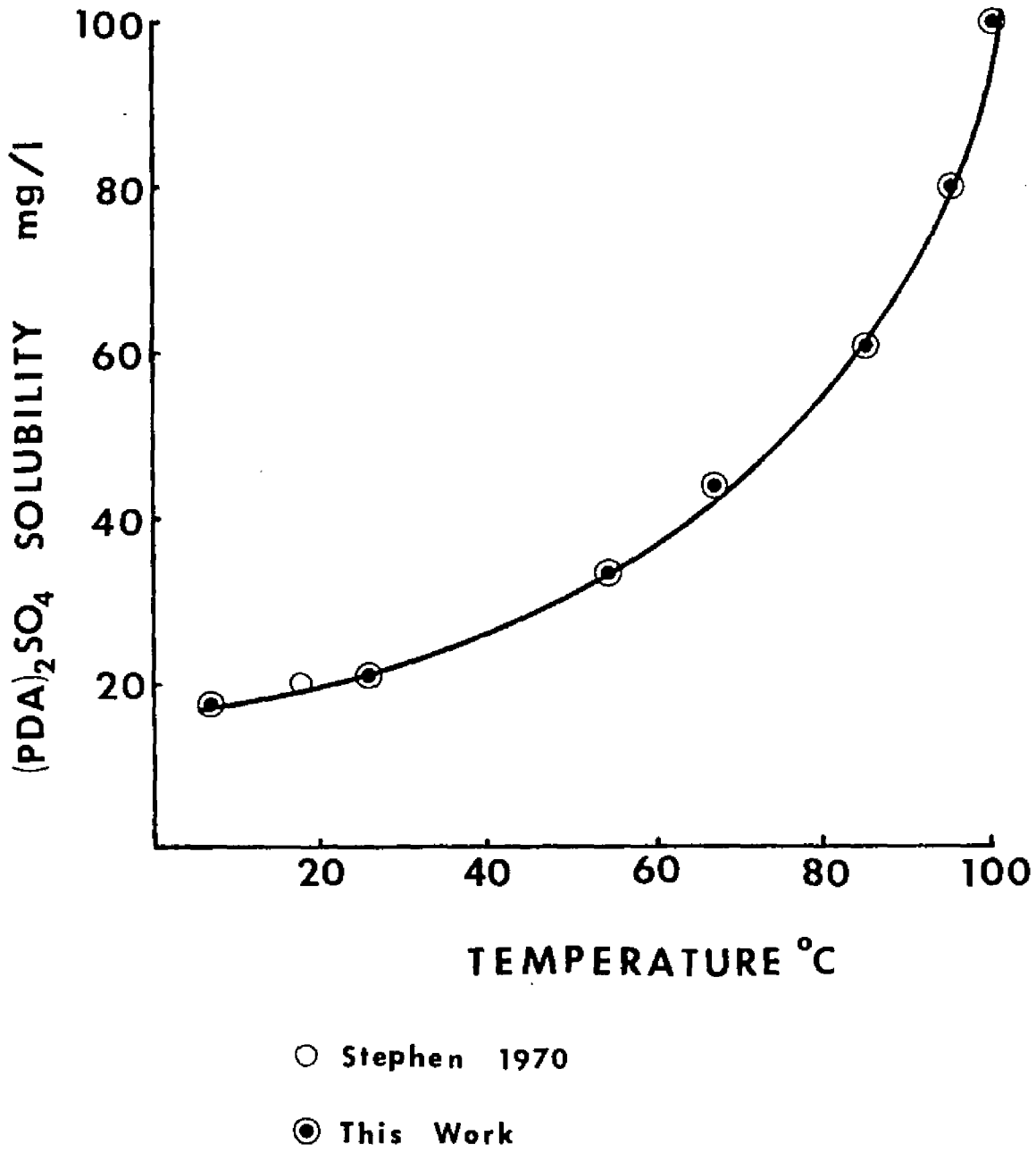
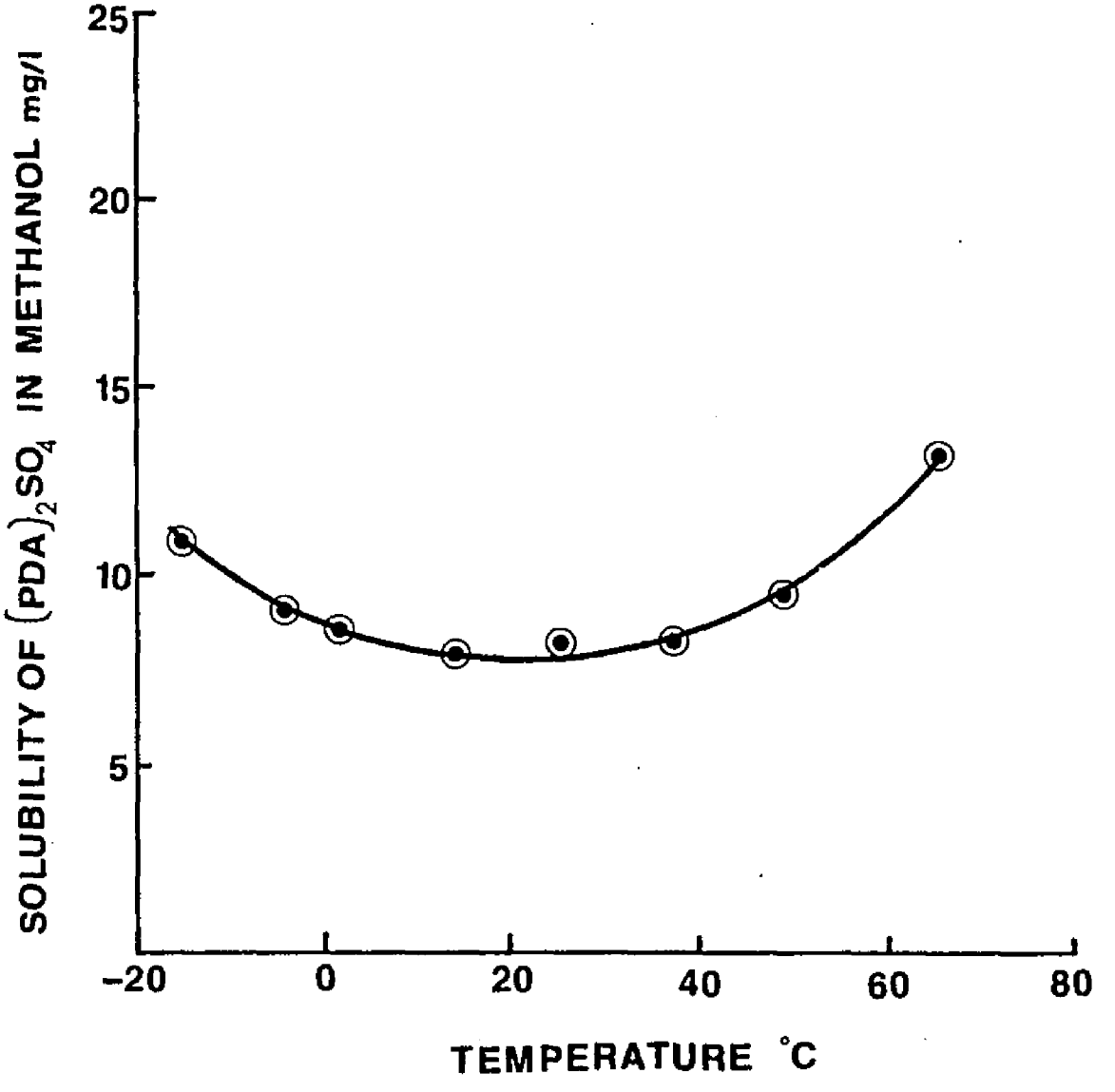

100
80
60
40
20
$(PDA)_2SO_4$ SOLUBILITY mg/l
20
40
60
80
100
TEMPERATURE °C
○ Stephen 1970
◉ This Work

FIGURE 21


SOLUBILITY OF $(PDA)_2SO_4$ IN METHANOL mg/l
25
20
15
10
5
-20
0
20
40
60
80
TEMPERATURE °C

of PDA-bromide we have some free amine, hydrogen ions, and bromide ions as well as some unionized PDA-bromide. The pH of a 0.016M solution of the salt was measured to be 5.80. The pH of an ammonium bromide solution of the same molarity was measured to be 5.80 also, and verified by calculation from available data. It would appear therefore, that the basicity of the organic amine is comparable to that of ammonia. Amounts of free amine present in solution is therefore insignificant, a conclusion that is also corroborated by the observation that PDA salt solutions are fairly stable while the free amine, if liberated by a strong base, is rapidly oxidized by air.

We know that equilibrium solubilities are only one of the factors that governs the minimum concentration at which visible precipitation occurs within a reasonable length of time. In no case does precipitation begin at the theoretical limit, as Von Weirman's law states, some degree of supersaturation is necessary. Compared to barium sulfate PDA-sulfate forms larger and more well defined crystals that are star-shaped.[469] It is impossible as well as impractical to use precipitant concentration as high as that normally used with barium chloride (saturated, $\sim$ 1.8M) because the solubility of PDA-bromide is much less. However, even with a 1% solution of the precipitant, at extremely low sulfate concentrations (0.05 ppm) the formation of PDA-sulfate is visible within 5 minutes, in contrast to saturated barium chloride, which does not produce any observable turbidity at this concentration within a reasonable period.

Further, in the particular methodology used in this work the solution is evaporated to dryness, making complete nucleation of PDA-sulfate possible. Under these conditions it is doubtful whether there is any better sulfate precipitant than the PDA cation.

B. SPECIATION BY CONTROLLING HUMIDITY AND POSSIBLE COMBINATION TECHNIQUES

Deliquescence points of some sulfate salts of atmospheric importance is listed in Table XVI. It would appear that by maintaining a $\sim$ 40% R.H. of the sample stream one would be able to speciate sulfuric acid and ammonium bisulfate from all other sulfates and bisulfates. It is doubtful whether present needs justify any further speciation without the advent of toxicologic data. If, however, further speciation is necessitated at a later date, the scheme due to Stine[472a] (Figure 2) may be applicable to this analysis technique.

C. THE NITRO SUBSTITUTED 2-AMINO PERIMIDINES

The free amine is very susceptible to oxidation. At first sight it is puzzling why this oxidation does not take place during treatment with concentrated nitric acid which is a very powerful oxidizing agent. Apparently the 2-amino group which is normally most susceptible to oxidation is protected by protonation during such treatment. In addition, this particular ring system must be very susceptible to electrophillic attack, the rate of nitration is very fast compared to most other ring systems.

In fact the slight reddish coloration produced on PDA-bromide impregnated filters during sampling of sulfuric acid aerosol

TABLE XVI

BULK DELIQUESCENCE POINTS OF VARIOUS SULFATES OF ATMOSPHERIC IMPORTANCE AT 20°C[522]

Compound	R.H. %
$NaHSO_4$	51
$KHSO_4$	86
NH_4HSO_4[96]	30-40
Na_2SO_4	86-93
$(NH_4)_2SO_4$	81
$ZnSO_4$	87
$MgSO_4$	91

generated by the stack generator is probably due to nitration also. Although pure oxygen is used as fuel, air is present in the stack due to the continuous aspiration and presumably at the high temperature of the oxy-acetylene flame, nitrogen reacts with oxygen to form nitrogen oxides to some extent. In the presence of sulfuric acid it is likely that some degree of nitration of the organic amine takes place and thus the observed coloration appears.

When PDA-bromide is refluxed with 1:1 nitric acid two trinitro monobromo derivatives are produced along with the tetranitro compound, with a bromine atom taking the place of a nitro group. Mechanistically it at first appears to be a puzzle since the bromide ion is a nucleophile and normally would not be expected to follow such a route. It seems more than probable that the ring bromination is not caused by a direct attack of the bromide ion but hydrobromic acid is formed in the highly acidic medium at first and this reacts to form nitrosyl bromide with nitric acid. It is established from dipole moment studies[309] that in nitrosyl bromide, bromine constitutes the positive end of the molecule. In fact, a relatively high positive charge is ascribed to the bromine atom which is not surprising in view of the high electronegativities of both oxygen and nitrogen. Therefore, the bromine substitution probably takes place via attack by nitrosyl bromide.

A sulfonic acid derivative from PDA-sulfate is therefore neither expected nor observed; an intermediate that would lead to an attack by the HSO_3^+ ion is clearly unlikely.

D. NEW AVENUES FOR WORK

Preliminary work has already shown that a trace nitrate determination method is feasible by the reversed reaction, i.e., the reaction of trace nitrate ions with PDA-sulfate dissolved in concentrated sulfuric acid. It is also possible that direct reaction with oxides of nitrogen in an acidified PDA-salt impregnated filter will lead to a fast, sensitive and specific colorimetric method for the determination of oxides of nitrogen in ambient air. The PDA cation itself is a powerful precipitating agent. It will precipitate otherwise difficult to deal with anions such as nitrate, acetate, citrate, formate, etc. Although none of these salts are as insoluble as the sulfate, they are quite insoluble by ordinary standards. Any of these ions, if present in a relatively interference free matrix,can be rapidly determined by precipitation as the PDA-salt, removal of excess reagent and followed by nitration.

The tetranitro compound is chemically the most interesting. The four nitro groups withdraw so much of the electron density of the ring that it results in some unusual properties. The ring protons are extremely acidic and quite labile as indicated by PMR studies. In addition, preliminary studies have shown that it forms charge-transfer complexes with many π-electron rich ring systems such as acenapthyne, 1,3,5-trimethoxy benzene, indole, etc. Such a complex formation is accompanied by a decrease in color intensity. There are recent studies attempting to relate the carcinogenic behavior of aromatic hydrocarbons with their π-electron

density. It is possible that a quick and dirty colorimetric method can be developed to roughly determine the total π-electron rich aromatic hydrocarbon loading of the atmosphere through the use of these compounds. In addition, the field of organic semiconductors is rapidly developing and the study of charge transfer complexes have proved to be very useful in this area.

PART IV

REFERENCES

"What do you know about this business?", the King said to Alice.

"Nothing," said Alice.

"Nothing whatever?" persisted the King.

"Nothing whatever," said Alice.

"That's very important," the King said, turning to the Jury.

- Lewis Caroll

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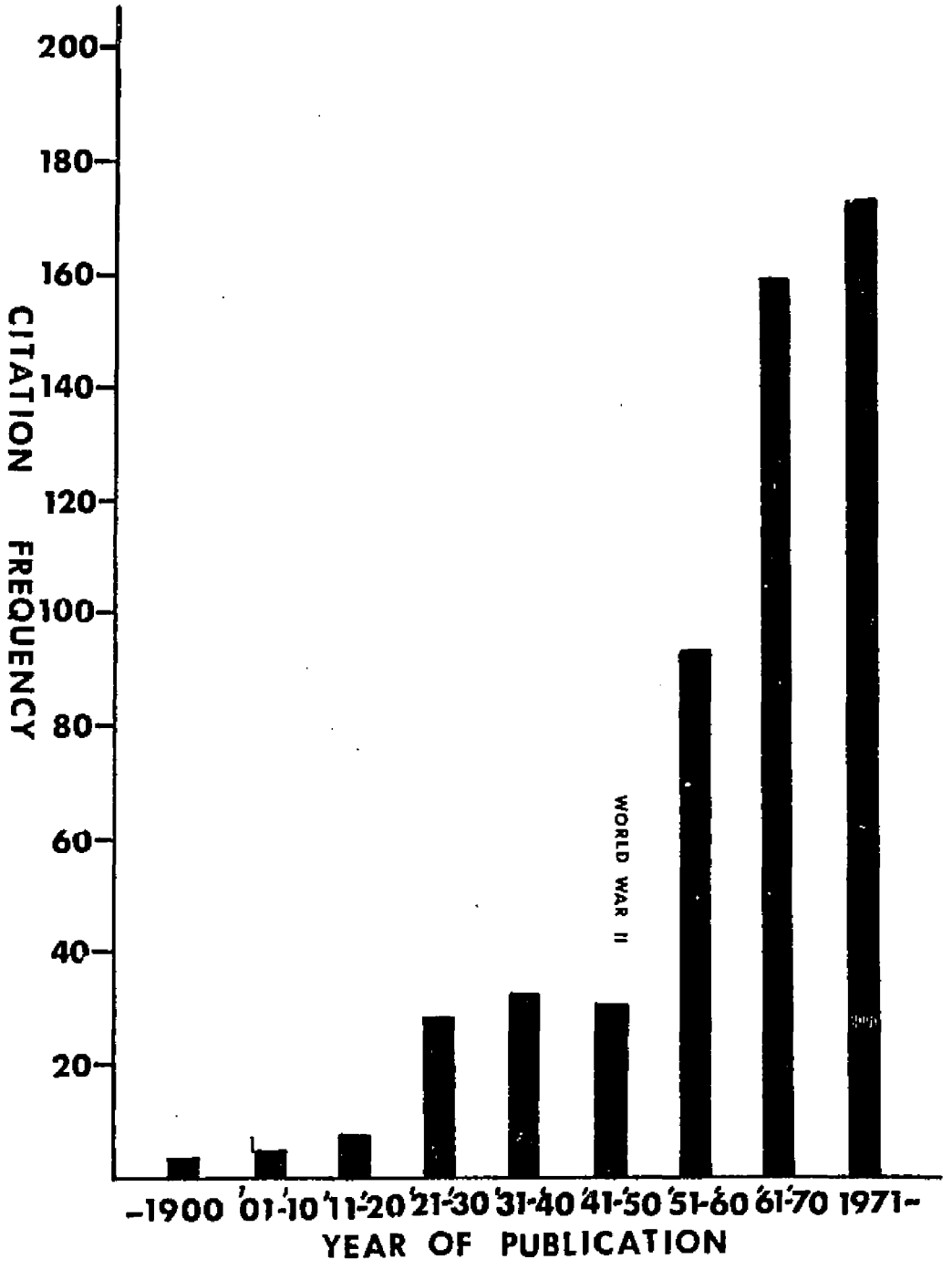
FIGURE 22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PART V

APPENDICES

"All generalizations are false, including the generalization that all generalizations are false."

- Old French Proverb

APPENDIX I

SYNTHESIS AND APPLICATION OF PERIMIDINYL AMMONIUM BROMIDE*

P. K. Dasgupta, G. L. Lundquist, K. D. Reiszner and P. W. West
Louisiana State University, Baton Rouge, LA 70803

Introduction: 2-Aminoperimidine hydrochloride was originally introduced by Stephen (1) as a turbidimetric reagent for sulfate offering excellent sensitivity. Since the method was plagued with interferences from various anions that also form insoluble precipitates with this reagent, field applications were limited. However, since the study and measurement of aerosol sulfuric acid and airborne sulfates became important, there has been a tremendous interest in this reagent. It was discovered that the reagent can be used with great success as an immobilizing agent in microdiffusive separation of sulfuric acid (2), that the resulting sulfate salt can be thermally pyrolysed to yield SO_2(3) which is easily measurable using the established West-Gaeke method (4), and that the reaction of aerosol sulfuric acid with a filter impregnated with this reagent is topochemical and free of interference from other particulate sulfates and metal oxides (5, 6, 7, 8). In fact, the latter (8) is currently under evaluation as the ASTM Standard Method. A colorimetric method involving the oxidation of 2-aminoperimidine sulfate is also almost complete (9). A very selective pyrolytic method for determination of sulfate in water at trace levels that employs this reagent is now completely developed (10).

* Variously referred to in the literature as perimidyl ammonium bromide, 2-perimidinyl ammonium bromide, PDA-Br.

Stephen synthesised the hydrochloride following Sach's original method (11). This method is quite cumbersome and McClure (12) developed a much simpler synthetic method to produce the hydrobromide salt. The account given here contains significant modifications of McClure's method. Changes in reaction medium and purification steps have been found to give a purer product in higher yield.

Experimental:

Reagents:

1.	Benzene	Technical Grade
2.	Cyanogen bromide	Reagent Grade
3.	1,8 Diaminonaphthalene	Technical Grade**
4.	Diethyl ether	Technical Grade
5.	Acetone	Technical Grade

Preparation: 1,8-diaminonaphthalene (DAN) may be purified by recrystallization from 1:1 ethanol-water (12); a much preferred method is two distillations under a 1.5 mm vacuum at 170 - 175°C. The purified DAN product has a pale yellow to white appearance. The reagent should be used immediately after purification.

The indicated amounts are for the preparation of approximately 100g of PDA-Br dihydrate. 72g of purified DAN is dissolved in 500 ml of benzene and 52g of cyanogen bromide dissolved in 500 ml of benzene. The latter solution is placed in an ice bath and the DAN solution added slowly with constant stirring. While monitoring the temperature,

** 1,8-diaminonaphthalene is almost white when pure, but the pure compound is highly susceptible to oxidation and aquires a purplish color rapidly. Since purification before use is necessary in any case, using a better grade of the reagent as the starting material has no advantage.

the mixture is removed from the bath and replaced alternately so that the temperature does not exceed 50°C. Below 20°C the reaction proceeds slowly so overcooling should be avoided. A pale tan product begins to separate immediately and finally the mixture becomes quite viscous. After 30 min. the mixture is set outside the bath, warmed to ~ 40°C if necessary, and set aside for another 30 min. to ensure complete reaction.

Purification: The product is filtered under vacuum in a large Buchner funnel and washed slowly with 50 ml of benzene, and then small volumes of acetone until the filtrate is colorless. One liter of water is brought to boiling and boiled for 10 min. to ensure removal of dissolved oxygen. The PDA-Br product is added to the water and stirred vigorously to help quick dissolution. The hot solution is filtered under vacuum through a bed of activated coconut charcoal. The hot filtrate is quickly transferred to a large erlenmeyer flask,. stoppered, and allowed to come slowly to room temperature whence beautiful needle-like crystals separate from the solution. The mixture is refrigerated at ~ 10°C to improve the yield and filtered. The product is recrystallized again in the above manner and the resultant product should be almost perfectly white. Any last tinges of color are removed by washing with a small volume of 1:1 ethanol : acetone.

The solid form of the reagent is PDA-Br $2H_2O$, which can be dried at 80°C for 4 hrs. to the anhydrous compound and this goes back to the dihydrate unless kept in a dessiccator (McClure found the form to be the dimer monohydrate). [Analysis. Calculated for C_{11} H_{14} N_3O_2Br: 44.02% C, 4.70% H, 14.00% N; found 44.13% C, 4.73% H, 13.98% N]. The white crystalline product has a m.p. of 265°C.

Discussion: Nucleophilic additions to cyanogen bromide are commonly preformed in polar solvents. But the use of benzene instead of dimethoxyethane (12) has advantages. First, the reaction temperature can be more carefully controlled and therefore the reaction is less violent. Secondly, the PDA-Br product is less soluble in benzene. Thirdly, benzene is more readily available and less expensive then dimethoxyethane. Further, like other ethers, the presence of peroxides in commercial dimethoxyethane aids in rapid oxidation of both diaminonaphthalene and PDA-Br, leading to undesirable intensely colored products, which often necessitate many more recrystallization steps.

The reaction is exothermic and careful monitoring is necessary to prevent the reaction from reaching explosive proportions. The heat of reaction is apparently related to the purity of DAN and solvent polarity. With pure, white DAN and in benzene medium the reaction proceeds slowly and with little heat liberation. Even a little warming is necessary to make the reaction go at a reasonably rate. The product is also purer and requires only one or two recrystallization (in the previous procedure (12) 6 recrystallizations were typical). The initial product may vary from off-white to tan depending on the purity of DAN. In sunlight, PDA-Br undergoes a slight discoloration, even pure PDA-Br should be stored in a brown bottle.

The use of acetone as a wash solution is also an improvement in the purification procedure. Impurities are quite soluble in acetone and PDA-Br is not, while product loss is observed with ether washing. Table I contains the solubility of PDA-Br in various solvents. The low solubility of PDA-Br in benzene demonstrates why it improves the product yield. An improved yield is observed by using water for the

recrystallization solvent. Previous recrystallizations were done in ethanol or methanol (12). The yield after purification is 70 - 75% as PDA-Br.

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TABLE I. Solubility of PDA-Br in various solvents

SOLVENT	SOLUBILITY[a]
Ethanol	2.4
Water	0.6
Acetone	0.1
Ether	0.3
Benzene	< 0.03
1,2 -Dimethoxyethane	0.1

[a] Solubility in g/100 ml at 26°C

APPENDIX II

DESIGN AND CIRCUIT EXPLANATION OF THE SPECTROPHOTOMETER COMPUTER INTERFACE

The available analog to digital converter (ADC) unit connected to the Nova 1200 Computer was a limited resolution device with a full scale capability of 10 volts. The output from the Beckman spectrophotometer was 100 millivolt full scale and was linear with transmittance as read on the instrument meter. The interfacing device therefore was basically an amplifier with a gain of 100 based on the 941 operational amplifier. In addition, the computer had to know when the spectrophotometer starts its scanning, and a pair of terminals are provided at the back of the Beckman DB which was open in any switch position other than scan. When the instrument was switched to scan position, these two terminals were shorted.

The schematic of the interface is shown in Figure 23. Normally the 941 operates on an inverted output mode, i.e., a signal of opposite polarity appears at the output because the inverting input is used. Problems were faced in using this configuration and therefore the amplifier was used with the non-inverting input (pin 3) receiving the signal from the spectrophotometer. The input resistor R_6 and Grounding resistor R_5 were chosen to be sufficiently high so that neither the output circuitry of the spectrophotometer was overloaded, nor the bias current for the 941 became excessively high. The gain was then selected by selecting a suitably high value for the feed-back resistor R_7. The gain was actually slightly higher than 100 (102.3) with the circuit components used and so the full scale output from the spectrophotometer itself was adjusted to give a full

SCHEMATIC OF INTERFACE : BECKMAN DB TO NOVA 1200

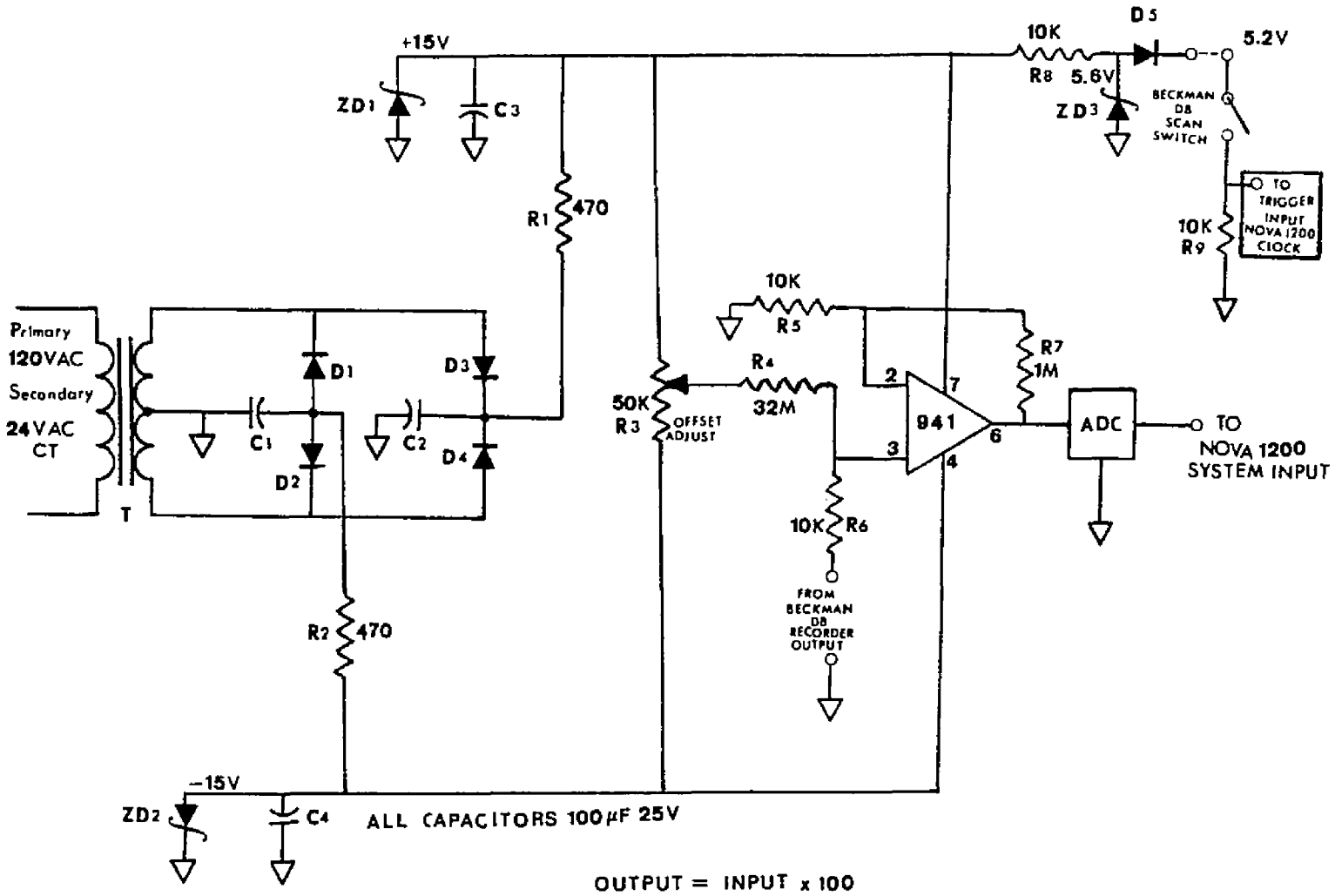

FIGURE 23

scale output of 10 volts at the amplifier output (pin 6).

Transformer T had a center tapped secondary and the 12V AC voltage obtained was rectified by the diodes D_1, D_2, D_3 and D_4 and filtered by the capacitors C_1 and C_2. The negative supply was tapped from the junction of D_1 and D_2 through R_2 and held at -15V by the Zener diode ZD_2; it was also further filtered by capacitor C_4. R_2 limits excessive current through ZD_2. Similarly positive voltage was obtained from the junction of D_3 and D_4 through R_1, filtered by C_3, and held at +15V by ZD_1. The positive supply was connected to pin 7 and the negative supply was connected to pin 9 of the operational amplifier. In addition, the positive supply was connected through R_8 to ground via zener diode ZD_3 which held the voltage at 5.6 volts at its cathode. R_8 limited the current through ZD_3. This voltage was dropped by another 0.4 volts by the forward drop of the diode D_5 so that 5.2 volts appeared at the cathode of D_5. This voltage is TTL (Transistor Transistor Logic - on which the Nova 1200 operates) compatible and was then fed into the trigger input of the system clock of the computer, via the scan switch of the Beckman DB. The trigger was grounded by Resistor R_9 and it was held at ground potential when the scan switch was not closed. On switching the instrument to scan position, voltage appeared across R_9 and the clock was triggered. Much higher values of R_9 were tried before and caused complications by false triggering, presumably due to the induced noise on the resistor.

Resistor R_3 and R_4 provided the offset voltage to the input of the operational amplifier, and R_3 was so adjusted that the output was zero when the input was grounded.

APPENDIX III

WESTSAS, WESTSAS2 AND THE MATHEMATICAL BASIS OF CALCULATING INDICATOR CONSTANTS FROM SPECTRAL DATA

Define: C_0 = concentration of the neutral species,

C_1 = concentration of the nonprotonated species

C_2 = concentration of the diprotonated species

$$K_1 = \frac{[H^+]C_0}{C_1} \qquad K_2 = \frac{[H^+]C_1}{C_2}$$

$$C_t = C_0 + C_1 + C_2$$

A_0 = absorptivity of the neutral species at a given wavelength λ

A_1 = absorptivity of the monoprotonated species at a given wavelength λ

A_2 = absorptivity of the diprotonated species at a given wavelength λ

A_t = observed absorbance.

Then:

$$C_0 = \frac{C_t K_1 K_2}{B} \qquad C_1 = \frac{C_t K_2 [H^+]}{B} \qquad C_2 = \frac{C_t [H^+]^2}{B}$$

where $B = K_1K_2 + K_2[H^+] + [H^+]^2$

$$A_t = C_0A_0 + C_1A_1 + C_2A_2$$

or

$$A_t = \frac{C_t}{B} [K_1K_2A_0 + K_2[H^+]A_1 + [H^+]^2 A_2]$$

Now, A_t and B are functions of hydrogen ion concentration while C_t, K_1 and K_2 are constants at all times and A_0, A_1 and A_2 are constants at a given wavelength.

For a given wavelength at a hydrogen ion concentration $[H^+]$;

$$A_{ti} = \frac{C_t}{B_i} [K_1K_2A_0 + K_2[H^+]_i A_1 + [H^+]_i^2 A_2]$$

or

$$A_{t_i} = \alpha_i A_0 + \beta_i A_1 + \gamma_i A_2$$

where

$$\alpha_i = \frac{C_t K_1 K_2}{B_i} \qquad \beta_i = \frac{C_t K_2 [H^+]_i^2}{B_i}$$

Now A_0 A_1 and A_2 can be calculated from α, β and γ by matrix methods.

WESTSAS2: With the help of initial crude approximations guesses were made at the values of K_1 and K_2. (Actually fairly good guesses could be made by assuming for example, that there is no neutral species at the lowest pH values or that there is no diprotonated species for the highest pH values.) For a given wavelength, the program computed a β and γ at various pH values and also calculated A_0, A_1 and A_2. By a general linear models procedure (GLM) the values of α, β, γ, A_0, A_1 and A_2 were altered around the calculated values to obtain the correlation with the input variable A_t for the whole pH range. These 'guestimate' values of A_0, A_1 and A_2 were calculated for a number of wavelengths and used subsequently by the main program WESTSAS.

WESTSAS: With the input values of the data matrix and best guesses at A_0, A_1 and A_2 this program started with the values guessed for K_1 and K_2 earlier and iterated them over two orders of magnitude in both directions in a non-linear least squares grid search to obtain the best fit with the input variable A_t. When this subroutine was finished another non-linear least square iterative

search procedure (Gauss-Newton) took over and the final best values were calculated. This procedure was repeated for several wavelengths to check the confidence limits of the data and alerted the programmer if the confidence limit fell below 95%.

APPENDIX IV

GLOSSARY OF ABBREVIATIONS

ACS	American Chemical Society
ADC	Analog to Digital Converter
AIHA	American Industrial Hygiene Association
APCA	Air Pollution Control Association
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
b_{sp}	Light Scattering Coefficient
CHESS	Community Health Environmental Surveillance System
CMR	Carbon Magnetic Resonance Spectroscopy
DME	Dropping Mercury Electrode
DSC	Differential Scanning Calorimetry
DTPA	Diethylene Triamine Pentaacetic Acid
EDTA	Ethylene Diamine Tetraacetic Acid
EPA	See USEPA
ESCA	Electron Spectroscopy for Chemical Analysis
EVI	Extreme Value Index
FPD	Flame Photometric Detector
FTIR	Fourier Transform Infra Red Spectroscopy
GLM	General Linear Models procedure
GM	General Motors Coporation
HGA	Heated Graphite Atomizer
ILAMS	Infrared Laser Atmospheric Monitoring System

IBM	International Business Machines Corporation
IR	Infra Red
LC_{50}	Concentration Lethal to 50% of Test Species
LOD	Limit of Detection
LPIR	Long Path Infra Red Spectroscopy
LSU/SNCC	Louisiana State University Systems Network Computer Center
MAC	Maximum Allowable Concentration
MAQI	Mitre Air Quality Index
MCAA	Mono Chloro Acetic Acid
MMD	Mass Median Diameter
NAPCA	National Air Pollution Control Administration
NMR	Nuclear Magnetic Resonance
NO_x	Oxides of Nitrogen
ORAQI	Oak Ridge Air Quality Index
OSHA	Occupational Safety and Health Administration
PAN	Peroxy Acetyl Nitrites
PAR	4-(2-Pyridyl Azo) Resorcinol
PDA	2-amino perimidine
PDA-	2-Perimidinyl ammonium
PFR	Pulmonary Flow Resistance
PIXE	Photon Induced X-Ray Emission
PMR	Proton Magnetic Resonance Spectroscopy
PTFE	Poly Tetra Fluoro Ethylene
RH	Relative Humidity
RRS	Remote Raman System

SAE	Society of Automotive Engineers
SCE	Saturated Calomel Electrode
SD	Standard Deviation
SEM	Scanning Electron Microprobe
SO_x	Oxides of Sulfur
SPADNS	3-(p-sulfophenylazo) Chromotropic acid
TLV	Threshold Limit Value
TSM	Total Sulfur Monitor
TSS	Total Soluble Sulfate
TTL	Transistor Transistor Logic
UK	United Kingdom
UN	United Nations
USDHEW	U. S. Department of Health, Education and Welfare
USEPA	U. S. Environmental Protection Agency
USSR	Union of Soviet Socialist Republics
UV	Ultra-violet
VDI	Verein Deutscher Ingenieurs (Union of German Engineers)
WHO	World Health Organization
WPCF	Water Pollution Control Federation
XPES	X-Ray Photo Electron Spectroscopy
XRFA	X-Ray Fluorescence Analysis

VITA

Purnendu Kumar Dasgupta was born in Calcutta, India on December 5, 1949. He attended Bankura Zilla School in Bankura, India and graduated in 1965.

He received his B. Sc. and M. Sc. degrees in chemistry, both from University of Burdwan, India, in 1968 and 1970, respectively.

In January, 1973 he entered the graduate school at Louisiana State University, Baton Rouge, Louisiana, where he is presently a candidate for the degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

Candidate: Purnendu Kumar Dasgupta

Major Field: Chemistry

Title of Thesis: Specific Determination of Airborne Sulfates and Sulfuric Acid

Approved:

Philip W. West
Major Professor and Chairman

James D. Ingraham
Dean of the Graduate School

EXAMINING COMMITTEE:

Buddhadeva

Robert V. Hansman

M. Lucy Ho

Date of Examination:

November 11, 1977